

CHEMICAL BONDING, ELECTRONIC STRUCTURE, AND PROPERTIES OF SMALL METAL CLUSTERS

Inaugural-Dissertation
zur
Erlangung des Doktorgrades
des Fachbereiches Chemie
der Freien Universität Berlin

vorgelegt von
GIANFRANCO PACCHIONI
aus Mailand
1984



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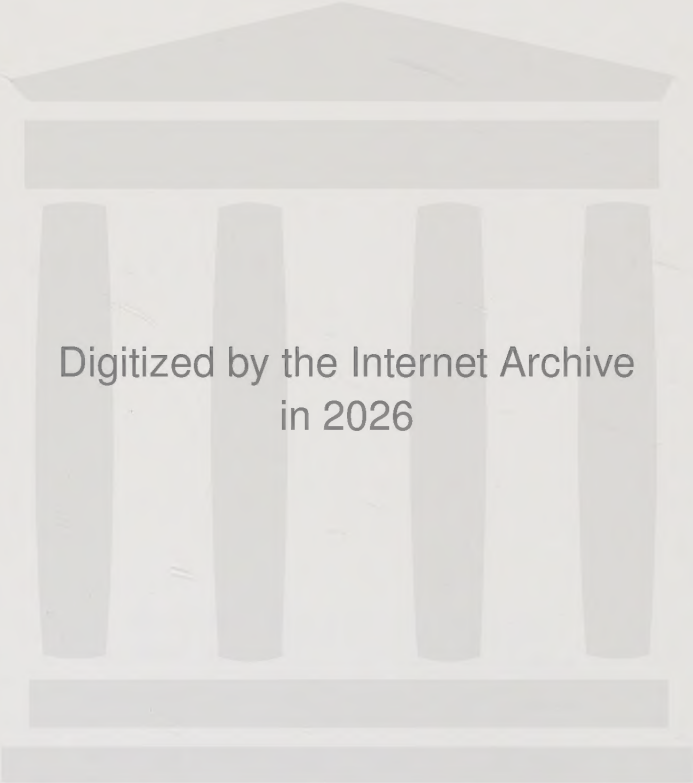
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1. Referent: Prof. Dr. J. Koutecký
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M e i n e r F r a u



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"Cuiusvis hominis est errare, nullius nisi insipientis
in errore perseverare"

(Cicerone, Phil., 12, 2, 5)

"I often say that when you can measure what you are speaking
about, and express it in numbers, you know something about
it; but when you cannot express it in numbers, your knowledge
is of a meagre and unsatisfactory kind"

(Lord Kelvin)

"In principle one could go ahead and calculate each molecule
... however even if the results were in excellent agreement
with experiment, the resultant predictability would not ne-
cessarily imply understanding. True understanding implies a
knowledge of the various physical factors, the mix of diffe-
rent physical mechanisms, that go into making an observable"

(R. Hoffmann, Acc. Chem. Res., 4,
1, 1971)

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1. P A R T I : I N T R O D U C T O R Y C O N C E P T S
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1.1 THE RESEARCH ON CLUSTERS: EXPERIMENTS AND THEORY

1.1.1 Why study small metal clusters?

The strong interest shown by both academic and industrial scientists in cluster research during the last decade is evident from even a cursory review of the scientific literature. For reasons of efficiency, industrial applications require metallic catalysts in a finely dispersed form, for which the active surface area for a given catalyst mass is greatly increased. Consequently, efforts in catalyst development have often been directed at producing even more finely dispersed materials. Particle sizes have progressively decreased from very large particles of $1000 \text{ \AA}$ to $10 \text{ \AA}$ and below (1).

Interest in clusters also arises from more fundamental reasons. Metal clusters, such as occur in metal vapor, have been proposed as aerosol precursors (2) or as the fifth aggregation state of the matter in addition to solid, liquid, gaseous and fluid states.

One of the major problems of cluster chemistry (hence catalysis) deals with the clustering steps leading to nucleation and with the single-atom-to-bulk-metal transition of the electronic properties. It is quite clear that the transition between the atomic state and the bulk is not a simple regular one that classical intuition might once have suggested. Rather complex changes are indicated both by theoretical calculations and by measurements. The question whether there is a gap or, instead, a progressive change from the molecular to the metallic state, and the question just when do the electronic properties of a metal cluster (such as cohesive energy, band structure, work function and magnetism) start to resemble those of the bulk, are still open. However, it is a current opinion that clusters with more than 100 atoms are needed to observe properties typical of the crystal (3,4).

Other theoretical incentives for investigating very small metal clusters arise from fundamental problems in the field of chemisorption and heterogeneous catalysis. For example, small



metal clusters have been proposed as models for the study of adsorbate-substrate interactions (5,6).

In these models, the chemisorptive bond is described in terms of a surface molecule (or atom) by coupling the adsorbate wave function to a limited number of neighboring metal atoms. Usually, theoretical studies of chemisorption employ a "surface fragment" (represented by two or more atoms) interacting with the chemisorbed molecule (or atom). The objective of these studies is to test the validity of the localized bonding by comparing the electronic and geometrical information obtained from calculations with experimental measurements on surface complexes.

This kind of approach entails, of course, many approximations. Firstly, the ionization potential of clusters is usually larger than the bulk work function and in clusters the Fermi level is not well defined. Thus electron exchange with adsorbate may be quite different for clusters and surfaces. Secondly, a cluster model cannot take into account the effect of the electron sea at the surface of the metal crystal. Finally, in the cluster concept one usually considers the interaction of a single adsorbed particle with the surface thus neglecting direct or indirect interactions between different adsorbed particles.

Some of these limitations may be removed, at least in principle, by the "embedding" model, which tries to remove the edge effects inherent in cluster modeling (7).

Despite these approximations it is now well established that metal clusters can provide some insight into the problem of heterogeneous catalysis and that they are certainly valid to investigate chemisorptive properties as a function of cluster size (8,9).

Further reasons to study the cluster problem come from the field of homogeneous catalysis and in particular of inorganic clusters. In the last 15 years the interest in the field of preparation and characterization of molecular complexes of transition metals containing homo- and heteronuclear metal-metal bonds has rapidly increased (10,12). Starting from a single metal atom

with its ligands it is now possible to prepare molecular clusters containing from 2 to 20 metal atoms bonded together in different geometries and surrounded by ligands(13).

The size of these molecules can approach that of very finely dispersed metallic catalysts. In one case we are dealing with very small clusters primarily stabilized by appropriate ligands, whereas in the other case the very small clusters are stabilized by interaction with a metal oxide support or trapped in the cavity of a zeolite or in an inert-gas-matrix.

The relations existing between the role of molecular clusters in homogeneous catalysis and that of naked clusters in heterogeneous catalysis as well as the nature and the strength of the metal-metal bonds in these compounds are still unclear.

In this respect, theoretical investigations have the prospect of playing an important role in the solution of the "cluster challenge".

1.1.2 Experimental preparation techniques

One of the most difficult problems in the field of small metal clusters is the preparation of samples suitable for experimental measurements. The size of a metal cluster can range from that of systems containing 10,000 atoms up to an atomic level limit, and consequently the experimental techniques are substantially different.

In the following the main experimental methods to prepare small metal clusters (with a size smaller than about $10 \text{ \AA}$) are briefly mentioned.

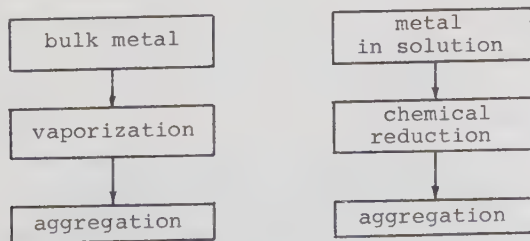


Fig. 1.1.1 - Experimental techniques to prepare clusters starting from bulk metals or from aqueous solution.

These techniques can roughly be divided into two categories. As shown in Fig. 1.1.1, in the first group are included the techniques in which the first step consists in the vaporization of the bulk metal followed by an aggregation process, while in the second group the metal is dispersed in solution as metal ion and the aggregation follows a process of chemical reduction.

1.1.2.1 Gas-phase clusters

Experimental data directly obtained on metal clusters in the gas-phase have the obvious advantage that they can be compared with corresponding theoretical data.

One possible way to obtain small well defined metal clusters consists of the Knudsen cell effusion method in conjunction with mass-spectrometric analysis (Fig. 1.1.2). Here a sample of the metal is vaporized at high temperature (about 3000 K) in the Knudsen cell. In the equilibrium gas over molten metal a small fraction of the polymeric species is present and mass spectrometry can be used to determine the polymer ratio as a function of temperature. Reaction enthalpies and dissociation energies are obtained by the third law of thermo-

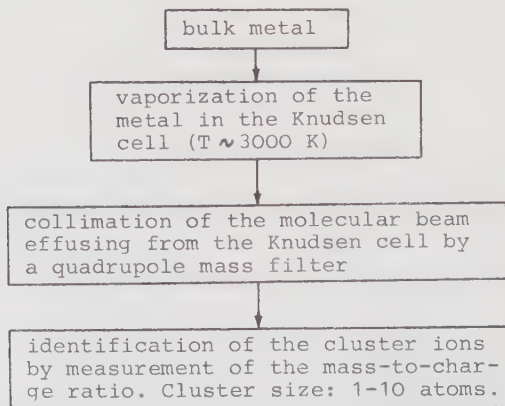


Fig. 1.1.2 - Metal clusters by Knudsen cell effusion method .

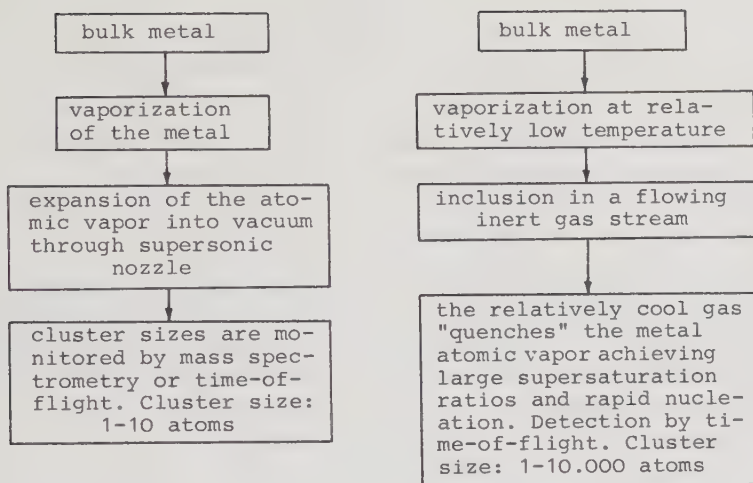


Fig. 1.1.3 - Metal clusters by gas aggregation technique.

dynamics (14). This method has been successfully applied to many elements and the dissociation energies of the clusters Ge_{3-7} , Sn_{3-7} , Pb_{3-4} , Bi_{3-4} (15), Cu_3 , Ag_3 , Au_3 (16), Li_3 and Li_4 (17,18) have been determined in this way.

A second technique widely applied in the last years involves the formation of clusters in vapor phase in a supersonic beam (19,20) (see Fig. 1.1.3a). The molecular beam is produced by expansion of the metal vapor through a supersonic nozzle into a region at much lower pressure. The gas cools and expands forming clusters. Cluster sizes are detected by mass spectrometry time-of-flight methods and clusters containing from 1 up to 20 atoms can be obtained.

Ionization potentials, binding energies and vibrational frequencies of small metal clusters and in particular of alkali metal clusters have been measured with this method (20,21).

A modified version of the "supersonic beam" method involves the "entrainment" of the cluster beam in an inert gas at lower

temperature (Fig. 1.1.3b). The relatively cool gas "quenches" the metal atomic vapor and causes a rapid nucleation of the cluster (22,23). Clusters of low-melting metals such as bismuth, tin, lead, iridium and antimony covering the size range from dimers to several hundred atoms have been generated in this way and detected by time-of-flight techniques.

Recently has been reported a modification of this method which makes possible to obtain sodium and copper cluster of smaller size (Na_x , $x < 65$, (24), Cu_y , $y < 29$ (25)).

The disadvantage of this method is that no physical measurements on separated beams have yet been reported because of the difficulty to separate single-mass fractions from the whole cluster population.

1.1.2.2 Matrix isolated clusters

Isolation of small metal clusters or of a single metal atom in inert matrices at very low temperatures (26,27) is one of the most powerful techniques to prepare clusters suitable for spectroscopic measurements.

In order to obtain single metal atoms a high-temperature metal vapor is mixed with a large excess of rare gas and the mixture is frozen onto a substrate at liquid-helium temperature. An alternative is to condensate the metal vapor at room temperature with solid matrices such as carbon or silicon dioxide (28-30).

The technique of cryophotoaggregation (31-35) has been developed to generate clusters within a matrix at low-temperature. In this process aggregation is obtained by selective UV or visible excitation of the atoms in weakly interacting low-temperature supports (Fig. 1.1.4). The method has been used to isolate many different homo- and heteronuclear metal clusters containing few metal atoms. Moreover, in this way also some highly coordinatively unsaturated transition metal cluster complexes such as $\text{M}_n(\text{CO})_m$ (36-38), $\text{Ni}_n(\text{C}_2\text{H}_4)_m$ (39,40), $\text{Pd}(\text{C}_2\text{H}_4)_n$ (41,42) and $\text{Ag}(\text{C}_2\text{H}_4)$ (43) have been isolated.

Determination of size distribution and cluster properties

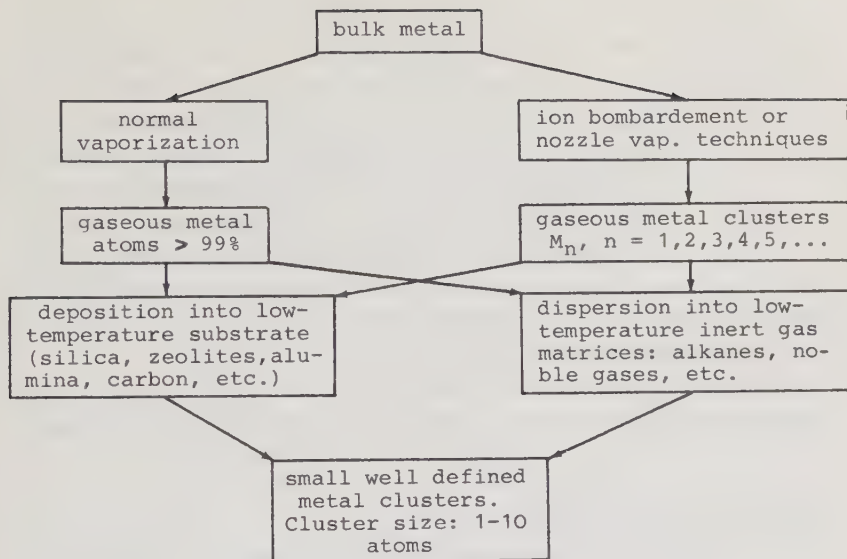


Fig. 1.1.4 - Metal clusters in low-temperature matrices.

are possible through spectroscopic analysis. UV-visible adsorption spectra have been reported for a large number of metal dimers and metal clusters such as Li_n (44), Na_n (45,46), Cr_n (33), Mo_n (47), Ni_n (48,49), Cu_n (48,49), Ag_n (50-55) and Bi_n (56-58). In addition, Raman experiments have been now performed on silver (55,59), nickel (27) and lead (60) clusters. Mössbauer (61,62) and MCD studies (63,64) on matrix isolated clusters have also been reported.

Extremely interesting are the ESR investigations on matrix isolated alkali metal clusters Li_n , Na_n and K_n (65-70), Mn_n (71), Cu_n (72,73) and Ag_n (74,75). In particular, the ESR measurements of Lindsay and coworkers (65-70) have provided new important information about geometry, electronic structure and spin distribution of Li_n clusters supporting the results of some previously performed theoretical investigations (76).

One problem in matrix-isolation spectroscopy is that of the

cluster-substrate interaction. It is often assumed that rare-gas-matrices are inert enough not to alter the physical and chemical properties of the isolated species. According to Ozin (31) "the weakly interacting supports commonly employed in matrix experiments are unlikely to seriously perturb the electronic and geometric properties of the entrapped metal cluster". However, both experimental (77,78) and theoretical (79) investigations on isolated atoms support the hypothesis that the matrix can change markedly the atomic properties and in some cases can change the electronic ground state of the atoms, as for matrix-isolated nickel atoms (80).

A more detailed discussion of the matrix-cluster interaction can be found in the recent review article of Ozin and Mitchell (81).

1.1.2.3 Supported metal clusters

Deposition of metal clusters onto planar substrates provides a relatively simple method to prepare well-defined and highly reactive metal clusters. Typical supports for deposition of clusters from aqueous solution are silica, alumina, carbon and zeolites. Single crystal surfaces have the advantage of chemical cleanness and well-defined crystallographic structure, whereas surface irregularities on amorphous substrates can cause variations in the cluster growth velocity.

The metal in solution is introduced in the support by various techniques, e.g., impregnation, adsorption, deposition, etc. This step is usually followed by hydrogen reduction and heat treatment to give supported metal clusters of size ranging from 5 to 100 Å (Fig. 1.1.5).

The high-resolution scanning-transmission electron microscopy (STEM) represents a powerful method to identify supported metal clusters. TEM images of Rh_5 clusters on silica have been obtained by impregnation of a silica support with an aqueous solution of RhCl_3 and reduction in situ with molecular hydrogen (82). Micrographs depicting isolated heavy atoms, dimers and larger clusters have appeared in the literature (82-84).

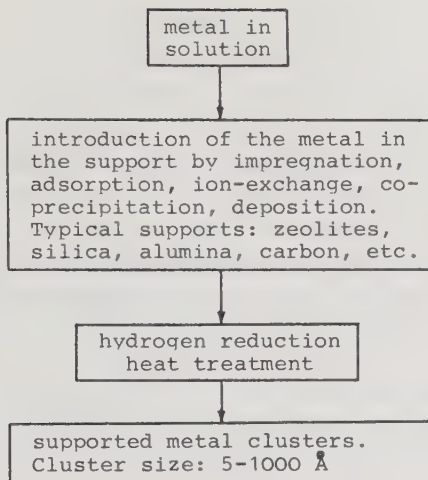


Fig. 1.1.5 - Supported metal clusters from aqueous solution.

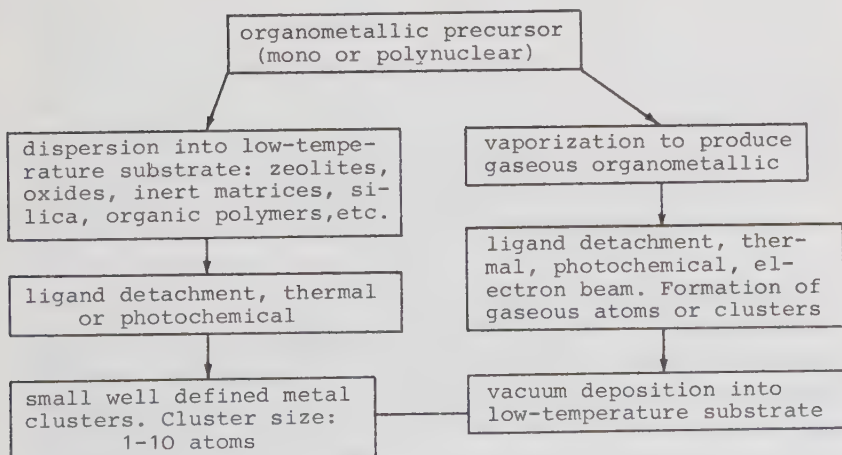


Fig. 1.1.6 - Supported metal clusters from organometallic precursors.

Cavities of zeolites represent also a kind of support for isolation of metal clusters. For instance, Ag_6 clusters included in the sodalite cavity of a sodium zeolite have been obtained from an aqueous solution of AgNO_3 . X-ray diffraction has shown that the Ag_6 clusters have an octahedral symmetry (85). In general, metal clusters encaged in zeolites represent appropriate systems to investigate the effects of particle size and support interaction on a supported metal catalysts.

Another method to obtain supported metal clusters is the dispersion of organometallic clusters onto low-temperature substrates (oxides, zeolites, organic polymers, silica, etc.) and their thermal or photochemical decomposition in order to obtain small well-defined naked metal clusters (Fig. 1.1.6).

An alternative is to vaporize molecular metal clusters in solid state and to induce ligand detachment through thermal or photochemical decomposition. The resulting gaseous metal clusters can be stabilized through vacuum deposition into low-temperature substrates (Fig. 1.1.6).

Supported metal clusters obtained in this way have shown a high catalytic activity. Ugo, Basset and coworkers (86) have found that during the thermal decomposition of the $\text{Rh}_6(\text{CO})_{12}$ cluster supported on silica to give the naked Rh_6 cluster, small amounts of hydrocarbons are formed. In particular, the Rh_6 cluster seems to catalyze C-O and O-H bond cleavages, and C-O, C-H and C-C bond formation to a limited extent (86).

The role of supported osmium carbonyls in the Fischer-Tropsch catalysis has been reviewed recently (87).

1.1.2.4 Organometallic clusters

Molecular metal clusters (or organometallic clusters) obtained by chemical synthesis provide a potential source of well-defined clusters displaying high catalytic activity (Fig. 1.1.7).

These compounds consist of a core structure of a defined number of metal atoms surrounded by stabilizing ligands, mainly carbonyls. They have fixed geometrical structures including me-

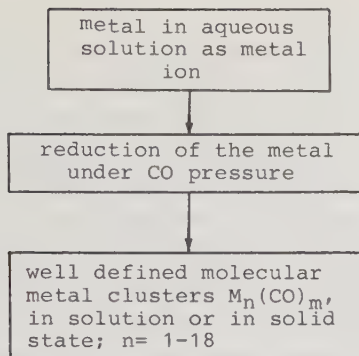


Fig. 1.1.7 - Organometallic clusters (molecular metal clusters).

tal-metal bonds. The evaluation of the strength of these metal-metal bonds is subject of discussion. In the past it was assumed that the metal-metal bonds could have strengths near those of the bulk metal but recent experimental (88,89) and theoretical (90,91) investigations support the conclusion that the metal cage is stabilized mainly through interaction with the ligand molecules.

Several review articles (1,4,10-13,92) have given details of synthesis, structure and properties of organometallic clusters so that here we report only the most important features of this class of compounds.

Firstly, molecular metal clusters can serve as models of chemisorbed molecules on metal surfaces (93-95). Structure and stereochemistry can be determined easily for these compounds but are established with difficulty for chemisorbed species apart from some simple cases such as CO and NO. Comparison of the spectroscopic data of clusters with those of chemisorbed species can provide qualitative information on the structure of the latter.

Secondly, organometallic clusters enable the generation of reactive monomolecular fragments of high catalytic activity by

thermal or photochemical decomposition of the cluster compound.

The third opportunity is catalysis by clusters. In particular, the structure of a cluster presents the possibility of consecutive reactions at different metal-atom-sites of the molecular cluster. This causes an unusual stereoselectivity and chemoselectivity in catalytic reactions.

Other illustrative examples of the extremely broad chemistry of molecular metal clusters are the relations between large metal clusters and metal particles, the use of supported clusters for catalysis (see previous Section), ligand fluxionality, changes in the cluster shape due to variations in electron count, activation of H_2 by clusters, cluster chirality, metal-metal bond reactivity, etc.

1.1.3 Rigorous ab initio calculations

Numerous investigations of metal clusters using various theoretical methods have been reported in the last ten years. In general, more sophisticated the method is, fewer are the atoms which can be treated. However, in comparison to the knowledge of the electronic structure of molecules or solids, very little is theoretically known about metal clusters. Thus, both simple and sophisticated methods can provide some insight into the field of clusters.

The information deduced from theoretical calculations is in general (with few exceptions) not easily available experimentally. Best geometry of a given cluster, bond lengths, stability, spin multiplicity of the ground state (and therefore magnetism), energy of the electronic transitions, ionization potentials, density of states, degree of hybridization, charge distribution, are all properties which can be obtained from calculations. Of course, the reliability of the results is strictly dependent on the quality of the theoretical treatment and on the details of the calculations.

A short review of some theoretical methods and of their application to the cluster problem has been reported by Messmer (9). Here, we mention only that the number of Hartree-Fock ab

1	2
H	He
1,008	4,00

3	4
Li	Be
6,94	9,01

11	12
Na	Mg
23,0	24,3

19	20
K	Ca
39,1	40,1

37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J	Xe
85,5	87,6	88,9	91,2	92,9	96,0	(99)	101,1	102,9	106,4	107,9	112,4	114,8	118,7	121,8	127,6	126,9	131,3

55	56	57-71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	unter	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132,9	137,4	178,3	178,3	181,0	183,9	186,2	190,2	192,2	195,2	197,0	200,6	204,4	207,2	209,0	210	(210)	(222)

87	88	89-
Fr	Re	unter
(225)	(226)	(227)

5	6	7	8	9	10
B	C	N	O	F	Ne
10,8	12,01	14,01	16,00	19,0	20,2

13	14	15	16	17	18
Al	Si	P	S	Cl	Ar
26,9	28,1	31,0	32,1	35,5	39,9

31	32	33	34	35	36
Ga	Ge	As	Se	Br	Kr
69,7	72,6	74,9	79,0	79,9	83,8

67	68	69	70	71
Er	Ho	Tm	Yb	Lu
167,3	164,9	168,9	173,0	175,0

97	98	99	100	101	102	103
Cf	Es	Fm	Md	No	Lw	
(251)	(254)	(255)	(256)	(257)	(258)	(259)

Fig. 1.1.8 - Experimentally (●) and theoretically (⊗) studied metal clusters. Diatomic molecules are not considered and only ab initio calculations have been reported.

initio calculations (including pseudopotential calculations) on metal clusters is still very small and mainly restricted to clusters of light atoms like Li or Be (see also Chapter 2.1 and 2.2). Among transition metal atoms only copper clusters have been intensively studied by different authors (96-99). Among other transition metal clusters only Ni clusters containing up to 6 atoms (100), Pd_3 (101) and Ag_3 (102) clusters were investigated by means of pseudopotential methods.

Up to now, the number of investigations in which the metal clusters have been used as models (mainly for chemisorption processes) far exceeds the number of studies in which the intrinsic properties of the clusters have been addressed.

However, the number of theoretical studies is increasing since the experimental techniques for determining geometries, properties and electronic structures of metal clusters are further developed (see for example the proceedings of some recent symposia on clusters (103-107)).

The Fig. 1.1.8 displays the metallic elements for which small metal clusters have been experimentally observed. Their number must be compared with that of elements whose clusters have been theoretically studied by means of ab initio quantum-mechanical treatments. From this figure it is evident that there are only few theoretical results in comparison to the experimental ones.

The necessity to have at disposition clear theoretical information for the interpretation of experimental results must be considered as an impulse to intensively study the electronic structure of small metal clusters.

1.2 THEORETICAL METHOD

1.2.1 Introduction

In this chapter the basic concepts of the theoretical method adopted are described. The investigation of small metal clusters has been done in the framework of the MO-LCAO (Molecular Orbital-Linear Combination of Atomic Orbitals) method. In this approach the wave function of the system is constructed in some form from molecular orbitals. The MOs in turn are approximated as linear combinations of basis functions which can be Slater type orbitals (STO), Gaussian type orbitals (GTO) or other basis functions.

The variational determination of the wave function of the system is done according to the Hartree-Fock procedure. If in the determination of the Hartree-Fock equations no integrals have been neglected or approximated and no empirical parameters employed, the method is generally referred as to an ab initio method.

It is well known that the bottleneck in going from theory to applications is located in the evaluation of one-electron as well as two-electron integrals, which number is growing as n^4 , where n is the number of basis functions of the system.

One way to reduce the size of the problem to be treated without introducing drastic approximations consists in the use of a pseudopotential method. The basic concepts of the pseudopotential theory are summarized in the next Sections.

1.2.2 The pseudopotential method

Determination of the electronic structure of chemical systems by solving Schrödinger equation is a difficult problem since the number of integrals to be computed grows very rapidly with the number of electrons and atomic orbitals present in the system. Only for small molecules it is possible to take into account all electrons, i.e., core and valence electrons.

In all other cases it is necessary to apply methods which consider explicitly only the valence electrons and which simula-

te the effect of the inner electrons by means of the potential generated by the nuclei and the core electrons. Such methods, as for example empirical and semiempirical methods in quantum chemistry of band calculations in solid state physics, have been successfully tested in the last twenty years, in particular in the field of solid state physics. However, their use is limited because of theoretical approximations: some matrix elements are neglected or parametrized in order to reproduce experimental values or other all electron calculations. On the other hand, the use of the pseudopotential theory allows to achieve a compromise between the computationally expensive all electron methods and the theoretically not well-defined semiempirical methods.

The fundamental idea is to replace cores, that are supposed to be chemically invariant when transferred from the atom to the molecule, by an analytical potential fitted at atomic level, facilitating in such a manner a detailed treatment of the chemically significant valence region of the molecules.

The first problem to be solved is that to describe separately different groups of electrons. Let us consider quite generally different groups of electrons A,B,C,... and suppose that a typical group has an antisymmetric wave function ϕ_R describing its N_R electrons. In the limit of zero interaction between the groups the Ψ of the system can be written as

$$\Psi(x_1, x_2, \dots, x_N) = MA \{ \phi_A(x_1, \dots, x_{N_A}) \phi_B(x_{N_A+1}, \dots, x_{N_A+N_B}) \} /1/$$

where A is an operator of antisymmetrization and M simply normalizes the wave function to unity in the usual way. If the electron groups are weakly interacting (as a result of their physical separation in space), a generalized product of the form /1/ may be a very accurate wave function because each factor may, at least in principle, describe correlation within the group of electrons to which it refers.

The fact that electrons in atomic and molecular systems can be decomposed into two characteristic types, "core" and "valence" electrons, is one of the basic and widely applied concepts

of modern chemistry. If it is assumed that all bonding processes involve only the valence electrons and that the core electrons remain independent from their chemical environment, then the core-valence separability can be expressed as

$$\Psi(x_1, x_2, \dots, x_N) = M_A \{ \phi_C(x_1, \dots, x_{N_C}) \phi_V(x_{N_C+1}, \dots, x_N) \} \quad /2/$$

where with ϕ_C and ϕ_V have been indicated the core and valence functions, respectively.

The first attempt to place this notion on a theoretical basis was done in 1930. However, only in 1959 Phillips and Kleinmann (108) rigorously showed that the explicit dependence of the wave function on the core electrons could be removed by the introduction of a non-local operator, the so called pseudopotential operator, in the Hamiltonian. If the total wave function can assume the form /2/ then the total energy of the system will be

$$E = E_C + E_V^{\text{eff}} \quad /3/$$

where E_C is the energy of the atomic core and E_V^{eff} is the energy of the valence electrons in the "effective field" generated by the core electrons.

The problem is just that to compute this term E_V^{eff} , and the solution is possible if the condition of "strong orthogonality" between the two functions ϕ_C and ϕ_V is assumed. The "strong orthogonality" requirement is more stringent than that imposed on ordinary spin-orbitals and takes the form

$$\int \phi_R^*(x_1, \dots, x_N) \phi_S(x_1, \dots, x_N) dx_i = 0 \quad (R \neq S) \quad /4/$$

This means that the result of integrating over any variable x_i common to both groups of functions must vanish identically for all the values assumed by the other variables $x_1, \dots, x_j, \dots$ etc. If this condition is respected the /2/ is the wave function of the system and the expression of the variational energy for a one-electron valence system takes the form

$$E = h_C + h_V + J_{CV} - K_{CV} \quad /5/$$

where h_C and h_V are the one-electron energies, J_{CV} represents

the Coulomb interaction energy between the charge distributions of the two groups of core and valence electrons. If we compare Eq. /5/ with Eq. /3/ it is possible to write $E_C = h_C$ and $E_V^{\text{eff}} = h_V + J_{CV} - K_{CV}$. The modifications of the valence wave function ϕ_V influence the three terms entering in the expression for E_V^{eff} but does not change E_C .

The condition of "strong orthogonality" is necessary not only to allow a separate treatment of valence electrons but also to avoid the variational collapse of the valence orbitals into the core orbitals during the iterative minimization of the energy of the system.

If all these conditions are satisfied, the Schrödinger equation takes the form

$$\left(-\frac{1}{2} \nabla^2 - \sum_C^{\text{core}} \frac{Z_C}{r} + \sum_C^{\text{core}} 2J_C - K_C + \hat{P}_C\right) \psi = E \psi \quad /6/$$

where, according to Phillips and Kleinmann (108), the pseudopotential operator $\hat{P}_C$ for a one-electron system satisfies the

$$\hat{P}_C \psi = \sum_C^{\text{core}} \left[E_V - E_C \right] \langle \phi_C | \psi \rangle \phi_C \quad /7/$$

Unfortunately, the use of the "exact" pseudopotential operator in a many-electron system results in a problem of comparable difficulty as the all electron problem.

Several methods for deriving pseudopotentials which circumvent the above difficulties have been described. In these approaches the valence Hamiltonian is written as a sum of one- and two-electron operators

$$H_V \approx \sum_i^{\text{val}} \left[h(i) + V_r(i) \right] + \frac{1}{2} \sum_{i < j} \frac{1}{r_{ij}} \quad /8/$$

From Eq./8/ it follows that the pseudopotential operator is a one-electron operator.

Two main categories of pseudopotential operators V_r are known, namely the "core projected" and the "angular projected" pseudopotential operators. The core projected operator can be generally written as

$$V_r^{\text{core}} = \sum_c W_c(r) \sum_A \sum_{c \in A} |\phi'_c \rangle \langle \phi'_c| \eta_c^A \quad /9/$$

Here η_c^A are parameters which take into account the energy difference between core and valence orbitals and ϕ'_c are approximate solutions of the true core orbitals ϕ_c of the free atom A.

The second group of model potentials, of angular projected type, has the general form

$$V_r^{\text{ang}} = \sum_A \sum_{l \in A} W_l^A(r_A) \hat{P}_l^A \quad /10/$$

In this expression the potential is written as a product of two terms, the first (W_l^A) depending on the distance r and the second ($\hat{P}_l^A$) representing the projector operator of the angular momentum defined on the subspace of spheric harmonics:

$$\hat{P}_l = \sum_{m=-l}^{+l} |Y_{lm} \rangle \langle Y_{lm}| \quad /11/$$

This second type of model potentials differs from the "core projected" one mainly for two reasons: 1) the pseudopotential operator is of the local type depending on r and 2) the core orbitals are not necessary in order to build up the projector operator.

The pseudopotential methods are characterized not only by the use of core-projector operators or not, but also by the different parametrization of the pseudopotential operator itself. The definition of calculations which employ pseudopotentials as "empirical" pseudopotential or as "effective core potential" is based on whether or not experimental atomic data are incorporated. Some authors make use of the terminology "ab initio" pseudopotential because the parameters have been determined by fitting all electron atomic calculations, but the inherent arbitrariness of all pseudopotentials makes this distinction less clear than for all electron calculations. A review of the pseudopotential methods employed in quantum chemistry is given in ref. (109).

The pseudopotential adopted for the present investigation, originally proposed by Durand and Barthelat (110,111), belongs to the group of angular projected model potentials. In particu-

lar, the valence pseudohamiltonian takes the form /8/ and the pseudopotential operator $V_R(i)$ is written as

$$V_R = -\frac{Z}{r} + \sum_1 w_1(r) \hat{P}_1 \quad /12/$$

where $Z = N_V$ (number of valence electrons) is the net charge of the ion built up from core electrons and atomic nucleus and $\hat{P}_1$ is the projector operator /11/. The radial part of the potential, $w_1(r)$, is strongly repulsive in the region near to the atomic nucleus in order to assure, without projector operator, the orthogonality between core and valence. The most general form of this term is

$$w_1(r) = \sum_i C_i r^{n_i} \exp(-\alpha_i r^2) \quad /13/$$

In the definition of the pseudopotential operator the two following conditions are to be respected:

- 1) the valence Hartree-Fock energy levels and the shape of the radial part of the "true" all electron valence orbitals ϕ_V must be reproduced as much as possible by the valence pseudo-orbitals ϕ_V for distances r larger than the core radii R_C ;
- 2) the radial part of ϕ_V must monotonically decrease for $r < R_C$.

Figure 1.2.1 gives the form of the radial part of orbital ϕ_V and the pseudo-orbital ϕ_V according to the previous criterion.

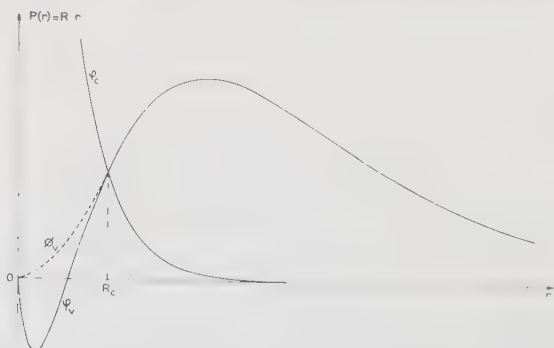


Fig. 1.2.1 - Radial parts of the all electron core and valence orbitals (ϕ_C and ϕ_V) and corresponding pseudo-orbitals (ϕ_C and ϕ_V).

The total atomic pseudohamiltonian /8/ leads to a variational solution of the valence Hartree-Fock-Roothan equations

$$\left[-\frac{1}{2} \nabla^2 + V_R + J_R \right] \phi'_V = H_V \phi'_V = \epsilon'_V \phi'_V \quad /14/$$

where J_R denotes the sum of the Coulomb and exchange operators related to the valence pseudo-orbitals. The potential V_R is chosen such that the solutions ϵ'_V , ϕ'_V of eq. /14/ coincide with the exact solutions ϵ_V , ϕ_V .

Practically, the parameters C_i and α_i in eq. /13/ are determined by minimizing the norm

$$||\Omega|| = \left[\langle \phi_V | \Omega^2 | \phi_V \rangle \right]^{1/2} \quad /15/$$

of the operator Ω defined as

$$\Omega = \epsilon'_V | \phi'_V \rangle \langle \phi'_V | - \epsilon_V | \phi_V \rangle \langle \phi_V | \quad /16/$$

The smallness of the norm measures the quality of the pseudopotential parameters.

The set of pseudopotential parameters adopted for the present calculations has been determined in the original work of Durand and Barthelat (111) in order to reproduce the valence orbital energies ϵ_V and the valence occupied orbitals ϕ_V of the double-zeta STO all electron calculations of Clementi and Roetti (112).

However, on going from atomic to molecular calculations (especially in the case of large molecules) the use of a STO double-zeta basis set is impracticable because of the well known difficulties in integral evaluation. The only economic way to perform molecular calculations consists in adopting a basis set of Gaussian type orbitals (GTO). However, a problem may arise since the pseudopotential (PP) parameters are consistent with an atomic STO basis set while GTOs must be used in molecular PP calculations.

This problem can be solved using an atomic basis set obtained by expansion of STOs into GTOs by means of one of the several procedures proposed in the literature (113-115). Since such an expansion can produce a loss of "optimum" characteristics of

the original STOs, an alternative is to derive the GTOs directly as variational solution of the PP atomic problem. This procedure has given very satisfactory results and has been applied to all atoms from Li to Kr (116,117).

The basis sets adopted here have been taken, if not differently specified, from these two latter references.

1.2.3 Electron correlation

The closed and open-shell SCF functions approximate many-electron interactions by assumption that each electron exists in an average field produced by all remaining electrons. The energy error resulting from this assumption is called the correlation energy. It is defined as the difference between the exact solution of the non-relativistic Hamiltonian and its expectation value in the Hartree-Fock approximation:

$$E_{\text{corr}} = E - E_{\text{HF}} \quad . \quad /17/$$

E_{HF} is the SCF limit (or Hartree-Fock limit) energy approached as the AO basis set approaches completeness.

The correlation energy, although generally is a small fraction of the total molecular energy, is of the same order of magnitude as the strengths of chemical bonds and of the electronic excitation energies. Moreover, the SCF wave function is not flexible enough to properly describe molecular dissociation. This is a particular problem when potential energy curves are considered.

One of the possible way to take into account correlation effects in atomic and molecular calculations is to make use of the configuration interaction (CI) procedure. The total molecular wave function is then represented as a linear combination of many-particle functions called configuration state functions (CSF). Each CSF is either a single Slater determinant or a linear combination of Slater determinants having the proper symmetry of the desired electronic state.

The CI wave function is defined as

$$\Psi_{\text{CI}} = \sum_{i=1}^n C_i \psi_i \quad /18/$$

where the coefficients C_i are determined through solution of the secular equation

$$(\mathbf{H} - E \mathbf{I}) \mathbf{C} = 0 \quad /19/$$

where the symmetric matrix contains the elements

$$H_{ij} = \langle \phi_i | \hat{H} | \phi_j \rangle \quad /20/$$

E and $\mathbf{C}$ are the eigenvalue and eigenvector of $\mathbf{H}$ for n roots corresponding to successive electronic states and $\mathbf{I}$ is the unit matrix. Usually, only the lowest one or few roots are considered due, for example, to basis set limitations or to the difficulty of selecting a set of CSFs appropriate for several roots.

In the present study the correlation effects have been taken into account in the framework of the multireference double excitation configuration interaction (MRD CI) method proposed by Buenker and Peyerimhoff (118,119).

The CI space in MRD CI consists from configurations arising by single and double excitations with respect to one or more main leading configurations (M). How to choose the main configurations is relatively easy since generally the most important configuration in the wave function is known from consideration of qualitative MO theory and additional configurations can be chosen on the basis of the magnitude of their coefficients in a relatively small CI.

The MRD CI method makes use of a configuration selection procedure and of a subsequent energy extrapolation for the evaluation of the final CI energy. The evaluation of the contribution of one generated excited configuration is done by solving the secular equation for the n main configurations M and this excited configuration. This process allows to obtain an estimation of the total energy contribution of one particular configuration to the final CI energy. Configurations with energy lowering below a given cut-off value (the threshold T) are not included in the final secular equation. The last step consists in the extrapolation of the total energy to the whole CI space ($T \rightarrow 0$). Of course, the magnitude of the threshold T influences the final result, but the goal is to effectively eliminate T as a parameter.

ter in the final results by means of a reliable extrapolation of the energy as T approaches zero.

The contribution of higher excitations than single and double to the final CI extrapolated energy can be evaluated according to the multireference generalization of the original Davidson formula (120):

$$E_{\text{full CI}} = E_{\text{ext}} + (1 - \sum_{\text{ref}} C_i^2) (E_{\text{ext}} - E_{\text{ref}}) \quad /21/$$

where E_{ext} is the extrapolated energy ($T=0$), E_{ref} is the energy resulting from the diagonalization of the CI matrix in the space of the main configurations, and $\sum_{\text{ref}} C_i^2$ is the weight of the main configurations in the final CI expansion.

The diagonalization of the CI one-electron density matrix gives the natural orbitals (NO) of the system. The corresponding eigenvalues are the occupation numbers of the NOs which, differently from the case of MOs, can assume non integer values between 0 and 2.

For some special cases, the investigation of the bonding characteristics of the various MOs or NOs has been carried out on the basis of the SCF or CI population analysis. Following Mulliken (121), the net atomic population of the atom A arising from the i -th normalized MO (or NO) $\phi_i = \sum_k C_{ki} \chi_k$, is given by

$$p_A^i = \sum_{l \in A} \sum_k n_l c_{li} c_{ki} \langle \chi_l | \chi_k \rangle \quad /22/$$

where n_l is the occupation number of the l -th MO (NO). The gross charge on a given atom is determined by summing the above over all MOs (NOs).

1.2.4 Reliability of the PP MRD CI procedure ^{*}

In the previous section the basic features of pseudopotential and configuration interaction methods have been presented.

The combination of a PP method with a procedure capable to take into account correlation effects is not a trivial problem.

^{*} The present section 1.2.4 has been partly published in the paper /4/ of the list of p. 201.

Few examples of PP calculations estimating valence-shell correlation are available and in general they are applied to the description of the molecular ground state (122-128).

In the following we compare the results obtained with the PP MRD CI method with some reference AE MRD CI calculations performed using basis sets of comparable quality. Three different problems have been chosen to test the reliability of the PP MRD CI procedure: the quenching process for the Na atoms in its $2P$ excited state by a CO molecule, the interaction of atomic hydrogen with a Li_2 cluster, and the study of the electronic structure of Al_2 and Al-H molecules.

In order to perform this series of calculations, the pseudopotential version of the IBMOL program, PSIBMOL, has been implemented in the Wuppertal-Bonn CI package (118,119).

1.2.4.1 Na-CO

The investigation of non-adiabatic processes is of fundamental importance in photochemistry. In recent years many experimental (129,130) and theoretical (131-133) studies have been reported in the literature. Among them, the quenching of excited alkali metal atoms by diatomic molecules such as N_2 , NO and CO represents a relatively simple model for the analysis of the electronic, vibrational and rotational energy transfer (133).

As a representative example of this type of chemical problems we have considered the interaction of a single Na^+ ion with a CO molecule: the potential energy curves for the ground and low-lying excited states of the Na-CO system have been determined.

In all CI calculations a selection threshold $T = 5$ hartree was employed and the size of the corresponding CI spaces to be diagonalized ranges from 1500 to 4000 configurations.

For the first set of calculations a GTO basis set of double-zeta type was chosen. For the PP calculations the $|4s4p|$ basis set B of ref. (116) was contracted to $|2s2p|$ for carbon and oxygen. This contraction scheme was adopted also for the 3s orbital of the sodium atom. Two 3p polarization functions have been added, giving rise to a $|4s2p/2s2p|$ PP basis set. The results obtained

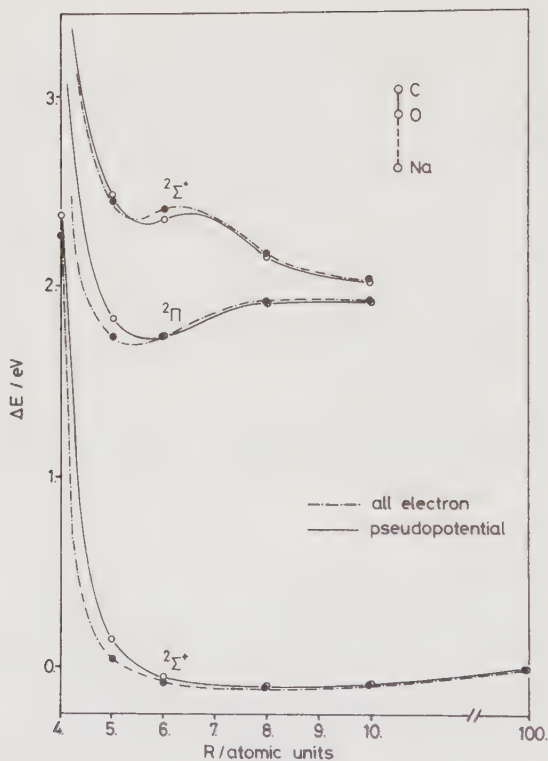


Fig. 1.2.2 - CI potential energy curves for the ground and first excited states of NaCO in colinear approach on the O-end. The C-O distance is fixed to the value of the free molecule (2.13 a.u.).

from PP calculations employing this basis set will be compared with the AE results obtained using Siegbahn's basis set (134) extended by the same polarization functions (133). With these basis sets the computed electronic excitation energy $\text{Na}(3^2\text{S}) \rightarrow \text{Na}(3^2\text{P})$ is 1.94 and 1.99 eV in the AE and PP calculations, respectively; these two quantities are to be compared with the experimental value 2.1 eV.

The potential energy curves for the interactions $\text{Na}(3^2\text{S}) +$

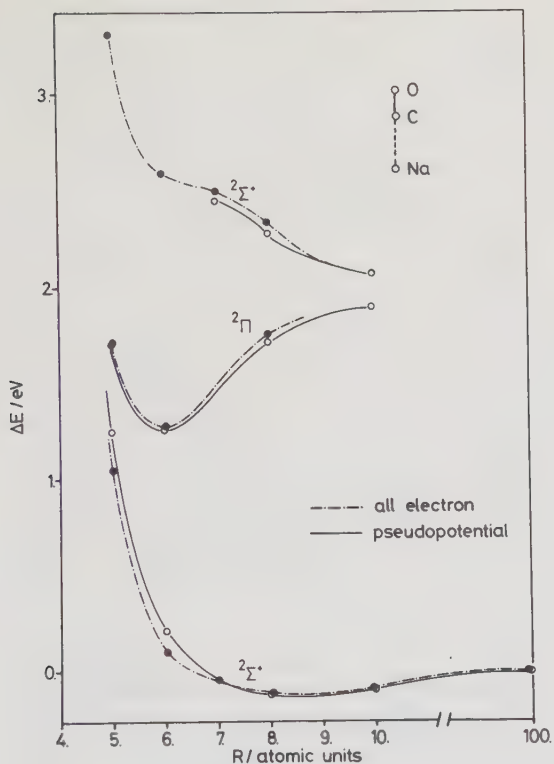


Fig. 1.2.3 - CI potential energy curves for the ground and first excited states of NaCO in colinear approach on the C-end. The C-O distance is fixed to the value of the free molecule (2.13 a.u.).

$\text{CO}(^1\Sigma^+) \rightarrow \text{NaCO}(^2\Sigma^+)$ and $\text{Na}(3^2\text{P}) + \text{CO}(^1\Sigma^+) \rightarrow \text{NaCO}(^2\Pi)$ have been obtained changing the distance R of the Na atom from the center of mass of the CO for two different colinear approaches: Na on the O-side and on the C-side of the CO molecule (see Fig. 1.2.2 and 1.2.3). The agreement between the AE and the PP curves is very good; a deep potential well is observed for the $^2\Pi$ excited state for both the Na-OC and Na-CO approaches. In particular, for this latter case the energetically lowest point of the curve

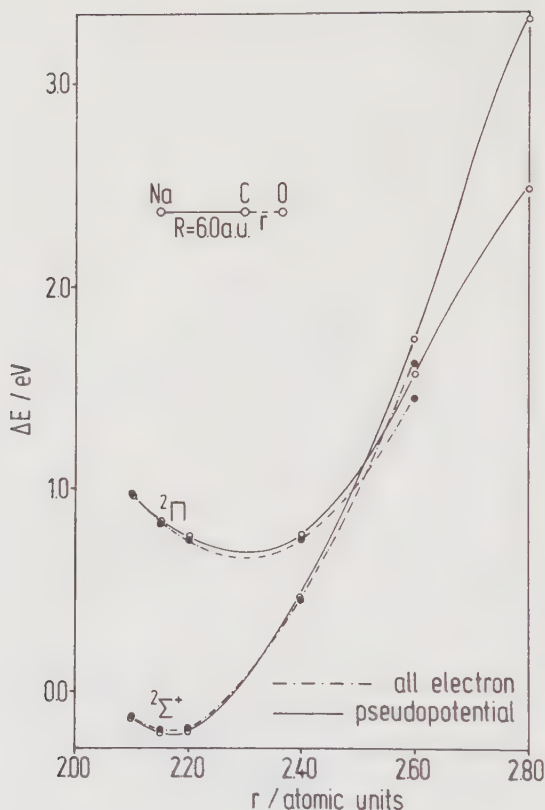


Fig. 1.2.4 - CI potential energy curves for the occurring crossing of the $2\Sigma^+$ and 2Π states of Na-CO when the C-O distance is stretched. The Na-C distance has been fixed to the value of 6 a.u.

(at a distance $R = 6$ a.u.) lies 0.73 eV below the asymptotic dissociation limit for this state.

The existence of a crossing of the first 2Π excited state with the $2\Sigma^+$ ground state of the molecule is crucial for the discussion of the quenching process. Very recently has been demonstrated that this crossing occurs when the relaxation of the CO molecule is allowed (133). Therefore, we have considered the

stretching of the C-O distance from 2.1 to 2.8 a.u. for the fixed Na-CO separation $R = 6$ a.u. . The PP results have been compared with the AE MRD CI curves of ref. (133) (see in particular Fig. 9 of ref. (133)). These AE results have been obtained with an AE basis set larger than that previously described including one s and one p diffuse function more on carbon and oxygen atoms and two diffuse s and one diffuse p function on Na atom (133).

In order to compare the position of the crossing point between $^2\Pi$ and $^2\Sigma^+$ states the same diffuse functions have been included in the PP basis set (C and O $|5s5p/3s3p|$, Na $|6s3p/4s3p|$). The PP and AE curves are given in Fig. 1.2.4. The expected crossing of the $^2\Pi$ and $^2\Sigma^+$ states is perfectly reproduced by the PP calculations. This means that discrepancies between AE and PP are not to be expected also if the atomic pseudopotential operator is used in connection with valence basis sets augmented by polarization functions taken from different AE calculations.

1.2.4.2 Li₂-H

The analysis of the interaction of the hydrogen atom with a small lithium cluster has been the subject of a great number of theoretical investigations, mainly because of considering these systems as simple models of very dispersed catalysts or of the chemisorption sites on metal surface itself. In the following we present the results of our investigation concerning the adsorption of the hydrogen atom on the bridge position of the Li₂ molecule. The Li-Li distance has been fixed to the value of 6.614 a.u., which is the Li-Li separation experimentally observed in the (100) face of the bcc lithium metal.

In both AE and PP CI treatments all configurations arising from single and double excitations with respect to the leading reference configuration are explicitly considered ($T=0$). The two lowest potential energy curves for the Li₂-H interaction are shown in Fig. 1.2.5 for the 2B_2 and 2A_1 electronic states. The AE curves have been computed with a $|8s2p/6s2p|$ basis set (135). For the PP calculations an uncontracted basis set, $|4s2p|$, was

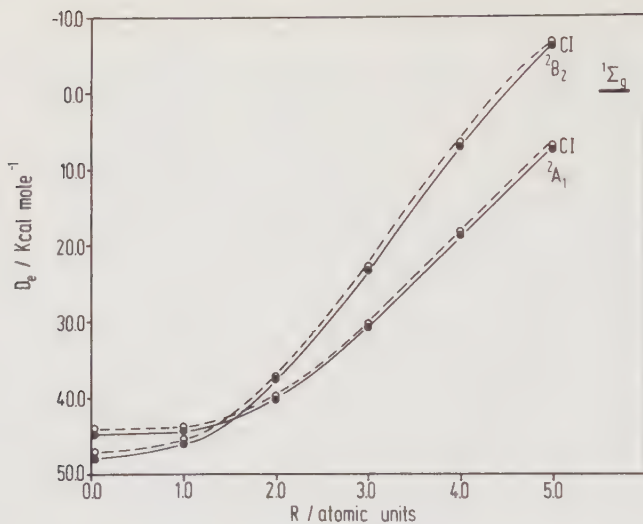


Fig. 1.2.5 - CI curves for the 2A_1 and 2B_2 states for the adsorption of hydrogen atom on Li_2 (100) cluster. The basis sets adopted for the Li atoms are: AE [8s2p/6s2p] (—), PP [4s2p] (---).

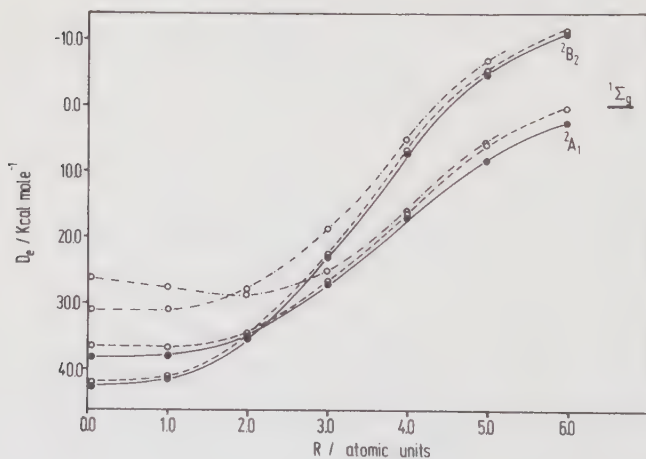


Fig. 1.2.6 - CI curves for the 2A_1 and 2B_2 states for the adsorption of hydrogen atom on Li_2 (100) cluster. The basis sets adopted for the Li atoms are: AE [6s1p/2s1p] (—), PP [4s2p/2s1p] (---), PP [3s1p/1s1p] (-·-·-).

adopted (basis set B of ref. (116)). Both these basis sets are of better quality than triple-zeta. The p-polarization functions at Li atom and the $|4s1p/2s1p|$ (136) basis set for the hydrogen atom are the same in the AE and PP treatments.

The AE potential energy curves are perfectly reproduced quantitatively by the PP ones; the two 2B_2 and 2A_1 electronic states cross each other for the same distances of the hydrogen atom from the middle point of the Li_2 molecule (1.55 a.u. and 1.53 a.u. in the AE and PP treatments, respectively). The chemisorption energies are 48.1 kcal/mole (AE) and 47.3 kcal/mole (PP) for the 2B_2 ground state, and 45.2 kcal/mole (AE) and 44.2 kcal/mole (PP) for the first 2A_1 excited state.

In a second series of calculations, the reference AE potential energy curves, obtained with a $|6s1p/2s1p|$ GTO basis set of single-zeta quality, have been taken from ref. (137). This small basis set has been originally chosen in ref. (137) in order to extend the calculations to larger systems. In PP we describe the valence region of the lithium atoms by means of the same set of 4s GTO previously mentioned, contracted into two s functions. The same p-function of the AE calculation has been added in order to take into account the polarization effects which are not negligible. The resulting potential energy CI curves are shown in Fig. 1.2.6, from which a good agreement between the results of the AE and PP treatments can be seen. This suggests that also double-zeta quality PP basis sets yield reliable results with acceptable computational costs.

On the contrary, a substantially different situation arises from the use of a smaller PP basis set, $|3s1p/1s1p|$ (116), contracted to a really minimal single-zeta type basis set. The two PP CI curves are shifted towards higher energies with respect to the AE ones in the minimum region. The computed binding energies for the 2B_2 ground state are 31.6 kcal/mole (PP) against the value of 42.1 kcal/mole obtained with the minimal AE basis set. For larger distances between the hydrogen atom and the Li_2 molecule these differences nearly disappear (Fig. 1.2.6).

The reasons for these discrepancies are to be looked for in

the deficiency of the PP basis set; in fact, in this case only one Gaussian function is used to describe the 2s atomic orbital of lithium. From the analysis of the $3a_1$ HOMO of the $\text{Li}_2\text{-H}$ system, obtained from the AE treatment, follows that the participation of the core orbitals of the lithium atoms in this MO is not negligible. This is true in particular in the region of the minimum. This means that at least two s functions are necessary for the description of the valence MOs of the $\text{Li}_2\text{-H}$ molecule, and this conclusion is well confirmed by the more reliable results obtained with the double-zeta $|4s1p/2s1p|$ PP basis set.

Finally, we report some estimated correlation energies for the 2A_1 excited state in the region of the minimum. For basis sets of comparable quality we have obtained: AE $|6s1p/2s1p|$ -0.0274 a.u., PP $|4s1p/2s1p|$ -0.0279; AE $|8s2p/6s2p|$ -0.0283, PP $|4s2p|$ -0.0284 a.u.. Therefore, the error between AE and PP treatments in the evaluation of the correlation energy is always smaller than 2 per cent.

1.2.4.3 Al_2 -

The understanding of the nature of the bond in Al_2 can be an useful tool in the study of larger Al clusters and of their interaction with small molecules. The only previously reported studies on the Al_2 molecule have been done for comparative purpose (138,139) or in the repulsive region of the potential energy curve (140). For the investigation of the Al dimer we have adopted four PP and two AE basis sets. The PP basis sets have been derived from the $|4s4p|$ GTO basis set of ref. (116) by means of two different contraction schemes and are the $|4s4p/2s1p|$, $|4s4p/2s2p|$ and the uncontracted $|4s4p|$. The fourth basis set has been obtained adding one d-polarization function to the $|4s4p/2s2p|$ basis set. The Gaussian exponent has been optimized at molecular level for the diatomic Al_2 ($\alpha = 0.22066$). The two AE basis sets, $|9s5p/3s2p|$ and $|13s10p/5s4p|$, are of single- and double-zeta type, respectively. The exponents and the contraction coefficients have been taken from ref. (141).

Table 1.2.1 - Results for the Al_2 molecule^a

	$^1\Pi_u$				$^3\Sigma_g^-$			
	SCF		CI		SCF		CI	
	$R_{\min}$	E_T/D_e	$R_{\min}$	E_T/D_e	$R_{\min}$	E_T/D_e	$R_{\min}$	E_T/D_e
PP(4s4p/2s1p)	5.50	-3.7778/8.3	5.51	-3.8293/19.3	5.20	-3.7663/1.2	5.17	-3.8244/16.3
PP(4s4p/2s2p)	5.46	-3.7821/11.0	5.48	-3.8490/20.2	5.07	-3.7681/2.2	5.01	-3.8435/16.8
PP(4s4p)	5.44	-3.7826/11.3	5.45	-3.8595/21.3	5.04	-3.7690/2.8	4.97	-3.8542/18.0
AE[1s10p/5s4p] ^b	5.41	-483.7230/12.3	5.42	-483.7926/22.1	5.05	-483.7079/2.9	4.99	-483.7863/18.2
PP(4s4p1d/2s2p1d)	5.28	-3.7923/17.4	5.23	-3.8984/26.0	4.80	-3.7805/10.4	4.70	-3.8955/24.2

^a All values are in a.u. except the dissociation energies which are in kcal/mole. The experimental ground state is the $^3\Sigma_g^-$ with the $R_e = 4.66$ a.u. and $D_e = 34.6$ kcal/mole

^b Only valence electrons are correlated.

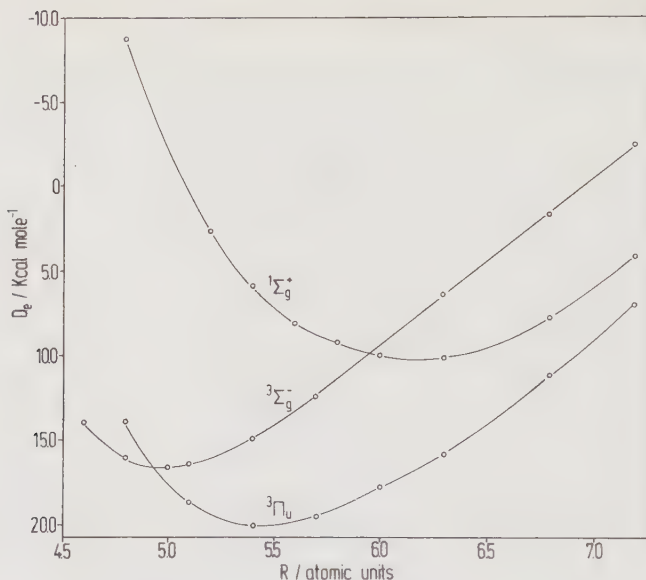


Fig. 1.2.7 - PP MRD CI curves for the three low-lying states $3\Pi_u$, $3\Sigma_g^-$ and $1\Sigma_g^+$ of the Al_2 molecule obtained with a $|4s4p/2s2p|$ PP basis set. The inclusion of d-polarization functions gives shorter equilibrium distances and larger binding energies (see Table 1.2.1).

The results for the two lowest triplet states of the Al_2 molecule are summarized in Table 1.2.1. The equilibrium separations and the binding energy obtained with the $|1310p/5s4p|$ AE basis set coincide with the PP ones obtained with the uncontracted $|4s4p|$ basis set. Moreover, the contraction of the three inner s and p functions, giving rise to the double-zeta type basis set $|4s4p/2s2p|$, practically does not alter the results which are very similar to the AE ones.

With this latter basis set we have performed a complete analysis of the potential energy curves for the three low-lying states of Al_2 , namely $3\Pi_u$, $3\Sigma_g^-$, and $1\Sigma_g^+$ (Fig. 1.2.7). For a distance close to the experimental equilibrium separation (4.7 a.u.) the $3\Sigma_g^-$ exhibits a minimum corresponding to a dissociation energy of about 16 kcal/mole. At 4.9 a.u. a crossing of the two

$^3\Sigma_g^-$ and $^3\Pi_u$ states has been found. The $^3\Pi_u$ state has the minimum around the distance 5.4 a.u. with a binding energy of 20 kcal/mole. The singlet state lies at higher energies and exhibits a shallow minimum (about 10 kcal/mole) at larger nuclear separation.

As already pointed out in the previous section, the further contraction of the p functions giving rise to the nearly single-zeta type basis set $|4s4p/2s1p|$ changes substantially the results producing too large interatomic distances and relatively small dissociation energies. It is worth noting that the AE treatment with the minimal basis set $|9s5p/3s2p|$ yields even less realistic results. This effect is to be attributed to a basis set superposition error.

However, all these theoretical treatments predict the $^3\Pi_u$ ($3p\sigma_g 3p\pi_u$) state of Al_2 to be more stable than the $^3\Sigma_g^-$ ($3p\pi_u^2$), in contrast to the experimental data (142). This result is in the same line with the other previously reported theoretical investigations (138-140) which also predict the $^3\Pi_u$ to be the ground state of the Al_2 molecule.

In order to obtain more realistic results we have performed a series of PP calculations adding one d-polarization function to the $|4s4p/2s2p|$ basis set. The results are reported in Table 1.2.1. The $^3\Pi_u$ is still the ground state, but the energy difference between the $^3\Pi_u$ and the $^3\Sigma_g^-$ states is only 1.8 kcal/mole. Moreover, the minimum of the $^3\Sigma_g^-$ potential energy curve is now very close to the experimental value (4.70 a.u. instead of 4.66 a.u.). The computed dissociation energy for the $^3\Sigma_g^-$ state, 24.2 kcal/mole, is still too small with respect to the experimental value of 34.6 kcal/mole.

The correction introduced in the results by the inclusion of one d function in the PP calculation is in the right direction, confirming that the discrepancies encountered are due to the poorness of the basis set and not to the PP method itself.

The use of basis sets including polarization functions of higher angular momentum and of large scale CI treatments is probably necessary in order to obtain a better agreement with the experimental results.

1.2.4.4 Al-H

An important requirement of the PP method is the capability to reproduce not only energetical data, but also other properties which are directly influenced by the quality of the correlated wave function. This point has been investigated in the case of the slightly polar AlH molecule. The calculations have been carried out with the previously described $|4s4p/2s2p|$ (PP), $|4s4p1d/2s2p1d|$ (PP) and $|13s10p/5s4p|$ (AE) basis sets for Al and $|4s1p/2s1p|$ basis set for the hydrogen atom (136).

Firstly, we compare the PP and AE results obtained without including d-function in the basis set. All single and double excitations generated from the starting leading configuration give rise to a CI space of the same dimension (108 configurations) in PP and AE. The corresponding computed correlation energies are -0.0510 (PP) and -0.0512 (AE) a.u. . The CI treatments are therefore strictly comparable and the results of Table 1.2.2 show that the PP approach is able to reproduce with a satisfactory accuracy the electronic properties determined from the AE wave function.

However, as in the case of Al_2 , some discrepancies are observed between theoretical and experimental (143) results (Table 1.2.2). Again, the inclusion of one d-function in the PP basis set improves the results giving a shorter equilibrium distance and a larger binding energy with respect to the result obtained with the $|4s4p/2s2p|$ PP basis set.

In Table 1.2.2 are also reported the values of the dipole moments and of the derivatives of the dipole moment functions. These values are compared with the results of the CEPA calculations of Meyer and Rosmus (144) performed with a large basis set. The high value of the dipole moment computed with the PP basis set without d-functions reflects the error in the determination of the equilibrium distance. The inclusion of the d-function reduces this effect, but the dipole moment remains very sensitive to the internuclear separation, as shown by the too large values of the derivative of the dipole moment function (Table 1.2.2).

Let us emphasize that the exclusion of the core-core and

Table 1.2.2 - Electronic properties of the AlH molecule

	PP MRD CI [4s4p/2s2p]	PP MRD CI [4s4p1d/2s2p1d]	AE MRD CI ^a [13s10p/5s4p]		
Equilibrium distance (a.u.)	3.22	3.17	3.16	3.11 ^b	
Dissociation energy (kcal/mole)	60.3	64.2	61.3	69.4 ^b	
Natural orbitals					
σ^+					
1	1.9685	1	1.9615	1	1.9681
2	1.9080	2	1.8785	2	1.9081
3	0.0300	3	0.0289	3	0.0292
4	0.0065	4	0.0064	4	0.0074
5	0.0017	5	0.0051	5	0.0040
6	0.0009	6	0.0018	6	0.0011
7	0.0003	7	0.0004	7	0.0004
		8	0.0003		
		9	0.0001		
		10	0.0000		
π					
1	0.0407	1	0.0515	1	0.0396
2	0.0011	2	0.0057	2	0.0011
3	0.0002	3	0.0007	3	0.0002
		4	0.0003		
Population analysis					
Al 3s	1.8161	1.7671	1.8601		
3p _w	0.0818	0.0960	0.1097		
3p _σ	0.7560	0.8777	0.7767		
3d	—	0.0900	—		
H 1s	1.3380	1.1614	1.3183		
2p _w	0.0022	0.0028	0.0022		
2p _σ	0.0059	0.0051	0.0060		
Dipole moment					
$\mu_z(D)$	-0.247	0.061	-0.064	-0.098 ^c	
$\mu'_z(D/\text{\AA})$	-4.46	-3.82	-4.20	-3.76 ^c	
Quadrupole moment					
Q_{xx}, Q_{yy}	-7.925	-7.958	-9.290		
Q_{zz}	-14.485	-13.387	-15.703		

^a Only valence electrons are correlated.^b Experimental values from Ref. 143^c CEPA values from Ref. 144

core-valence correlation can play a non negligible role on electronic properties such as dipole and quadrupole moments.

1.2.4.5 Discussion

The results of the PP MRD CI method applied to a number of various systems which have been presented in the previous sections are encouraging because of the excellent agreement with the results obtained with the AE methods.

The errors in the evaluation of equilibrium bond distances, dissociation energies and electronic distribution are in general

very small. On the other hand, it has been shown that the PP MRD CI approach is able to describe in a satisfactory manner quantities which are very sensitive to the choice of the basis set and to the inclusion of correlation effects.

The estimate of the correlation effects with the PP MRD CI procedure can be considered very successful ; in fact, it is not possible to exclude a priori that a pseudopotential operator determined from atomic SCF calculations will not generate undesired results when transferred into molecular configuration interaction calculations.

In particular the influence of correlation effects on bond lengths and dissociation energies of ground and excited states of the molecules are very similar in AE and PP treatments. A correct description is to be expected in all cases where an adequate choice of the basis set is made. The importance to built up the GTO basis set as variational solution of the atomic PP problem has been widely demonstrated (116,145), but the contraction scheme to adopt deserves some special care (146). It has been shown, for example, the failure of a PP minimal basis set to reproduce quantitatively the results of the corresponding AE CI calculations due to the small but important contribution of the core atomic functions. However, already the PP basis set of double-zeta quality represents a reasonable alternative to the larger uncontracted basis set and yields the same results as accurate AE treatments.

To summarize, the PP MRD CI approach seems to be rather versatile, giving reliable results in very different fields. It represents a well-grounded theoretical treatment since the pseudo-hamiltonian operator is built up in such a way that the variationally determined pseudo-orbitals coincide as much as possible with the true Hartree-Fock atomic orbitals in the valence region. The method seems to be applicable for the study of the electronic structure of molecular systems containing any atom of the periodic table.

2. PART II : ELECTRONIC STRUCTURE
OF SMALL METAL CLUSTERS
=====

2.1 ALKALI METAL CLUSTERS[‡]

2.1.1 Introduction

Small alkali metal clusters have been theoretically studied quite intensively because the number of electrons which should be considered in the calculation is not too large, in particular when Li clusters are considered. For this reason, among alkali metal clusters, Li clusters have been the subject of a large number of investigations while the available literature on Na and K clusters is still rather poor.

A variety of more or less sophisticated theoretical methods has been adopted for the study of this class of clusters ranging, for Li e.g., from semiempirical CNDO (147-150) or extended-Hückel (151-152) to diatomic-in-molecule (DIM) (153-155), valence bond (VB) (156) and X_α (157) methods. More accurate ab initio calculations have also been done on alkali metal clusters and in the following we summarize some of the most important results obtained in this way.

In a pionering SCF investigation, Janoschek (158) considered the potential curves for the approach of two Li_2 molecules and found the T-form of Li_4 (Fig. 2.1.1) to be stable with respect to the dissociation into two Li_2 molecules.

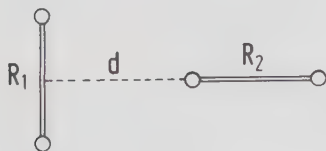


Fig. 2.1.1 - The T-form of alkali metal clusters.

[‡] The present chapter has been partly published in the papers /1/ and /8/ of the list of p. 201.

Stoll and Preuss (159-160) have studied Li aggregates using the Hartree-Fock technique and adopting pure spherical Gaussian functions. Chains, layers and three-dimensional structures were considered, with the finding that chains are favoured for small sizes. Various forms of Li_4 were considered in the SCF investigation of Marinelli et al. (161) but the use in all these works (158-161) of basis sets where p-functions are not included makes the results questionable.

In the all electron study of Fantucci and Balzarini (162), on the contrary, a STO-3G basis set including one p-polarization function was adopted for the analysis of the electronic structure of small Li clusters (up to Li_9). According to this study, the chain structures are not favoured. This result may be understood in terms of the role of 2p orbitals. The most stable structures are planar for clusters containing up to five Li atoms and in particular rhombic Li_4 was found to be more stable than the more compact tetrahedral arrangement. Above this size, stable structures preserve a C_{5v} axis for six atoms (capped pentagon) and seven atoms (bicapped pentagon), while most stable Li_8 and Li_9 clusters were obtained by capping the octahedric substructure. A possible mechanism of the crystal growth from Li_2 up to Li_9 has also been reported in this work (162). Moreover, the increase of the cluster size is accompanied by an increase of the cohesive energy (as measured by the binding energy of the cluster) and by a decrease of the ionization potential (162).

Correlation effects have been taken into account for the first time in the study of Kendrick and Hillier (163) on the two lowest states of Li_3 . An even more accurate SCF-CI calculation was done by Martin and Davidson (164) on the analogous states of Na_3 adopting a large basis set including p and d polarization functions. The study of Li_3 was reconsidered by Gerber and Schumacher (165) using the non variational CEPA approximation. All these studies have pointed out that the 2B_2 and 2A_1 low-lying states of Li_3 (for the C_{2v} symmetry) deviate by rather small amounts from the E' state of equilateral D_{3h} symmetry (163-165).

The CEPA approximation was used by Beckmann et al. (166) for the investigation of small Li clusters. The rhombus was confirmed to be the most stable Li_4 . Large scale CI calculations adopting basis sets of different flexibility were performed in the all electron MRD CI study of Beckmann et al. (135) on Li and Na tetramers. In this work the typical biradical feature of square and tetrahedric Li_4 and Na_4 clusters and the large influence of the spin coupling on the stabilities of Li and Na tetramers was shown. The same method of ref. (135) was adopted by Beckmann (167) for the investigation of the triangular form of Li_3 and by Beckmann and Koutecký (137) for the study of a series of Li_n clusters ($2 \leq n \leq 10$) which can be considered as sections of (100) and (110) surfaces of bcc Li crystal lattice.

In this work states of different spin multiplicity have been considered and it has been found that correlation effects are very important for the determination of the ground state of the cluster. A majority of Li clusters investigated in ref. (137) exhibits lowest singlet and lowest triplet states with almost degenerated energies. A similar analysis for Li_6 clusters modeling the fcc crystal lattice was done by Plavšić et al. (168) but the most stable Li_6 cluster was found to be the mono-capped pentagon, in agreement with the results of ref. (162). Finally, and unrestricted Hartree-Fock (UHF) investigation of multibody non-additive effects in small Li clusters has been reported by Del Conde et al. (169).

All the studies previously described have been performed by means of all electron calculations. However, the extension of accurate all electron SCF-CI calculations to larger metallic aggregates or to clusters of heavier alkali metal atoms, like Na or K, is extremely difficult to be carried out. The adoption of pseudopotential methods facilitates the study of these systems.

Li clusters containing up to 32 atoms have been considered in ref. (170) by means of a PP SCF method. A slow convergence of some properties like density of states, valence band width and ionization potential to the values characteristic of the

bulk metal was observed (170). A combination of a PP scheme and a density-functional approximation for the correlation energy was adopted by Flad et al. (171) to study equilibrium geometries and electronic properties of Na clusters containing up to 8 atoms. It was found that, as for Li tetramers, also for Na_4 the rhombic form is very stable even if in competition with a T-shaped form (Fig. 2.1.1). Moreover, the experimental ionization energies of Na_n clusters have been well reproduced as well as the alternancy in their dependence on n (171). The same approach has been adopted also for the study of small clusters of Na and K (128, 172) and, more recently, of their cations (173).

A different PP method was applied from Car and Martin (174) to the investigation of neutral and singly ionized small Li_n and Na_n clusters ($n = 2-4$).

Because of the small number of valence electrons, small alkali metal clusters or dimers have been frequently chosen to test the validity of more sophisticated pseudopotential approaches taking into account some effects which up to now have not been explicitly included in this theoretical approach.

In particular, three points of general interest have been the subject of intensive studies: a) the core-valence correlation (174-176), b) the polarization of the atomic core in molecular systems (172, 174, 175, 177, 178) and c) the relativistic effects (179, 180). The consideration of these effects can improve significantly the agreement between theoretical and experimental values, in particular for heavy atoms. Most of PP calculations previously discussed as well as our present approach do not make use of these corrections. However, even if core-valence correlation and core-polarization effects are not considered, the agreement between PP and AE calculations is satisfactory and the general results are qualitatively valid.

2.1.2 Computational details and basis set specification

For the investigation of alkali metal dimers and clusters two kind of GTO basis sets have been adopted. A minimal basis set consisting of three Gaussian functions (basis set A of ref. (116)) has been used in the case of the Li_2 molecule in order to test the effects produced on the electronic properties by the use of a small AO basis set. All other calculations have been done adopting a $|4s2p|$ and a $|4s2p1d|$ basis sets with exponents optimized at atomic level. The 4s Gaussian functions for Li, Na and K correspond to basis set B of ref. (116) and p and d functions were added to account for polarization and angular correlation effects. Exponents and contraction coefficients of these basis sets are given in Table 2.1.1.

Table 2.1.1 - Basis sets for Li, Na, K

	Orbital	Exponent	Contraction coefficient
Li	s	1.379040	-0.028913
		0.552155	-0.125042
		0.072625	0.588495
		0.027655	0.504195
	p	0.28	1.0
		0.07	1.0
	d	0.05	1.0
Na	s	2.665920	-0.012140
		0.443434	-0.136049
		0.058254	0.635192
		0.023284	0.455062
	p	0.8	1.0
		0.075	1.0
	d	0.12	0.62
		0.05	0.46
K	s	0.645239	-0.014015
		0.221749	-0.216504
		0.038473	0.686946
		0.016539	0.443486
	p	0.325	1.0
		0.023	1.0
	d	0.07	1.0

The basis set for PP molecular calculations must be flexible enough in the valence region in order to respond to the changes occurring upon molecule formation. Non-negligible lowering of the binding energy results from the use of contracted basis sets and therefore, according to Dunning (181, 182), uncontracted basis functions have been adopted to perform the calculations.

The details of the MRD CI calculations, e.g. selection threshold and number of leading configurations used, number of generated configurations, etc., are given in the description of the Tables reporting the results. As a general criterion all those configurations which contribute for more than 1 per cent to the final CI expansion are chosen as main configurations (M). If not differently specified, only one main configuration and selection threshold $T=0$ have been employed.

2.1.3 Alkali metal dimers

In Table 2.1.2 are reported the results for the optimized interatomic distances, binding energies per atom and ionization potentials obtained with a full PP CI method for the three dimers Li_2 , Na_2 and K_2 . These results are compared with other PP calculations which recently appeared in the literature (126, 128, 171, 173) and with all electron and experimental values (19, 21, 183-187) (see Table 2.1.2). The ionization potentials have been computed as the difference between the charged and the neutral species.

In the case of Li_2 the effect of the contraction of the basis set was analyzed performing calculations with a small basis set $|3s1p/1s1p|$ whose orbital exponents are taken from ref. (116). The contraction coefficients were optimized at molecular level on Li_2 . As mentioned in the previous section, such a small contracted basis set fails to give an interatomic distance and a binding energy close to the experimental values. Also the contraction of the two inner s Gaussian functions (basis set $|4s1p/3s1p|$) reduces the value of the binding energy of about 7 per cent with respect to the uncontracted calculation.

Table 2.1.2 - Results for Li_2 , Na_2 and K_2 ^{a)}

	Method and basis set	Binding energy per atom (kcal/mol)	R_e (bohr)	Ionization potential (eV)
Li_2	PP MRD CI [1s1p]	7.71	5.40	5.25
	PP MRD CI [3s1p]	9.70	5.15	5.02
	PP SCF [4s2p]	1.92	5.25	4.36
	PP MRD CI [4s2p]	10.49	5.09	5.11
	PP MRD CI [4s2p1d]	11.11	5.12	5.19
	PP CIPSI [3s2p1d]	10.95	5.16	—
	PP DF [11s5p]	10.04	5.11	—
	AE SCF [6s2p]	1.82	5.27	4.34
	AE MRD CI [6s2p]	9.85	5.08	—
	AE MRD CI [6s2p] ^{b)}	10.29	5.10	5.14
	AE MRD CI [7s3p]	10.17	5.05	5.12
	experiment	12.33 ^{c)}	5.05 ^{c)}	5.15 ^{d)}
Na_2	PP SCF [4s2p]	-0.60	6.04	4.05
	PP MRD CI [4s2p]	6.71	6.01	4.69
	PP MRD CI [4s2p1d]	7.70	5.99	4.75
	PP CIPSI [3s2p1d]	7.84	6.04	—
	PP DF [12s8p]	7.84	5.71	—
	AE SCF [7s3p]	1.45	—	4.37
	AE MRD CI [7s3p] ^{e)}	8.48	5.81	4.98
	experiment	8.40 ^{f)}	5.82 ^{f)}	4.93 ^{g)}
K_2	PP SCF [4s2p]	-1.95	7.93	3.26
	PP MRD CI [4s2p]	3.54	8.20	3.74
	PP MRD CI [4s2p1d]	4.77	7.96	3.79
	PP CIPSI [2s2p1d]	4.72	8.07	—
	PP CIPSI [3s2p2d]	5.07	7.93	—
	PP DF [9s4p]	4.70	7.27	—
	experiment	5.88 ^{h)}	7.38 ^{f)}	4.06 ^{h)}

a) PP MRD CI: pseudopotential with MRD CI; PP CIPSI: pseudopotential with CIPSI[126]; PP DF: pseudopotential with density functional method [126]; AE MRD CI: "all-electron" ab initio with MRD CI.

b) The CI procedure is applied only on 2s electrons.

c) See refs. 183 d) See refs. 185-186

e) The CI procedure is applied only on 3s electrons,

f) See ref. 187 g) See ref. 19 h) See ref. 21

On the contrary, the use of primitive Gaussian functions in the PP procedure produces results which are in agreement with all electron calculations, but which differ from the experimental ones. In particular the binding energies are too small and the interatomic distances too large. This becomes more marked on going from Li_2 to K_2 .

Maynau and Daudey (126) attribute these discrepancies to the fact that the influence of the core region on the single valence electron of alkali metals is not accounted for

explicitly in the PP method. It is difficult to assess the importance of core-valence correlation in these systems; in the case of Li_2 , e.g., we compare our PP results with two all electron calculations in which correlation among all electrons and correlation of only 2s electrons are considered. The results show that the differences in the properties are not too large (see both AE MRD CI calculations with $|6s2p|$ basis set in Table 2.1.2). In the case of the Na_2 molecule, the better results of the all electron calculation, in which the CI procedure was applied only to 3s electrons, are probably due to the more flexible basis set $|7s3p|$ used in this calculation with respect to the $|4s2p|$ basis set employed in the PP procedure.

The empirical pseudopotential with density functional estimation of the correlation effects (PP DF procedure of Preuss et al. (128)) is assumed to include core-valence correlation since the pseudopotential is built up in such a way that reproduces the experimental energies of the one-valence-electron ions. No relevant differences in stability appears from the use of this empirical pseudopotential (128) in place of the "ab initio" pseudopotential adopted in our calculations (Table 2.1.2). However, the better values of the interatomic distances found in ref. (128) can perhaps be attributed to the very large basis set used.

These considerations suggest that the inclusion of the core-valence correlation alone cannot give a sufficient improvement of the theoretical results with respect to the experimental ones but of course this point needs further investigations. More marked is the effect of the introduction of d-functions in the basis set. In fact on going from Li_2 to K_2 our results show that the improvement in the binding energy per atom is 0.62, 0.99 and 1.23 kcal/mole, respectively.

2.1.4 Li_4 clusters

The study of some geometrical arrangements of Li_4 clusters whose stability is strongly influenced by the spin coupling has been chosen as a severe test for the reliability of the present PP approach. The singlet and triplet states of the

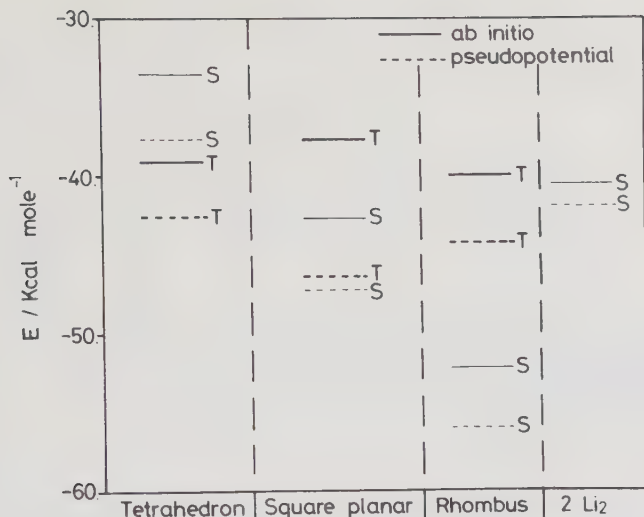


Fig. 2.1.2 - Singlet and triplet energies of tetrahedral, square planar and rhombic Li_4 cluster as computed with AE MRD CI (—) and with PP MRD CI (---). The singlet state energy of two Li_2 molecules is drawn at the right side of the figure. For computational details see Table 2.1.3 .

rhombic, square and tetrahedral Li_4 clusters are calculated with $|4s2p|$ AO PP basis set for the geometries predicted on the basis of the all electron optimization.

The general trend of the stability for the different Li_4 clusters in the singlet and triplet states is pictured in Fig. 2.1.2 and agrees well with the corresponding results of all electron calculations with $|6s2p|$ AO basis set (see also Table 2.1.3).

For the square arrangement a large energy dependence of the lowest singlet and triplet states on correlation effects and on the basis set was found (135). SCF and MRD CI calculations performed with a relatively small PP basis set $|4s1p|$ predict the triplet state of the biradical square arrangement

Table 2.1.3 - Properties of Li_4 clusters^{a)}

	Method and basis set	Binding energy per atom (kcal/mol)		ΔE (singlet - triplet)	Ionization potential ^{b)} (eV)	
		singlet	triplet		singlet	triplet
rhombus	PP MRD CI [4s2p] c)	14.26	11.07	12.76	4.61	4.05
	AE MRD CI [6s2p] d)	13.04	9.89	12.86	4.54	3.98
planar square	PP MRD CI [4s2p] c)	11.80	11.64	0.60	4.77	4.74
	AE MRD CI [6s2p] d)	10.63	9.43	4.83	4.67	4.46
tetrahedron	PP MRD CI [4s2p] c)	9.40	10.62	-4.90	4.08	4.29
	AE MRD CI [6s2p] d)	8.35	9.77	-5.68	3.99	4.24

a) The calculations have been performed for the following AE optimized geometries : rhombus: side length 5.82 bohr, angle 127°; planar square: side length 5.52 bohr; tetrahedron: side length 5.76 bohr.

b) Li_4^+ cations have been calculated with the SCF MOs of the Li_4 clusters.

c) 6M/1R treatment with $T = 0.4 \mu\text{hartree}$.

d) 6M/1R treatment with $T = 0.4 \mu\text{hartree}$ and correlation among all electrons.

to be lower than the corresponding singlet one and only the use of a more flexible basis set in a 6M/1R MRD CI treatment allows to obtain the singlet ground state. In this respect the results of the present PP calculations are to be considered very satisfactory even in the case of the square-planar cluster since the same qualitative ordering is obtained from both the AE and PP calculations. In our PP approach we obtain binding energies which are 4-5 kcal/mole lower than those obtained from AE calculations (Fig. 2.1.2). A similar result was obtained for the Li_2 molecule when we compare the PP binding energy per atom (10.49 kcal/mole) with the AE value of 9.85 kcal/mole obtained by correlating both 1s and 2s electrons. This discrepancy nearly disappears when we consider the AE binding energy of 10.29 kcal/mole derived from correlating 2s electrons only.

In order to test the possibility to adopt the pseudopotential method for the investigation of larger clusters, we have done some PP calculations adopting a relatively small basis set $|4s1p/2s1p|$ on rhombic Li_4 and on a Li_8 cluster section of the fcc Li crystal lattice which was found to be the most stable Li_8 cluster on the basis of AE calculations performed with a nearly minimal basis set ($|6s1p/2s1p|$).

Table 2.1.4 - Comparison of AE and PP results for Li_4 and Li_8 clusters^{a)}

	Singlet			Triplet			E_B/n kJ/mol	$E_B - E_B^b$ (eV)
	E_{SCF}	E_{CI}	E_{corr}	E_{SCF}	E_{CI}	E_{corr}		
Li_4 AE	-29.5314	-29.5912 ^{c)}	0.0598	-29.5225	-29.5732 ^{d)}	0.0507	51.9	0.5
Li_4 PP ^{e)}	-0.8003	-0.8631 ^{c)}	0.0628	-0.7947	-0.8466 ^{d)}	0.0519	50.6	0.5
Li_8 AE	-59.1088	-59.2167 ^{c)}	0.1079	-59.0909	-59.1912 ^{c)}	0.1003	63.2	0.7
Li_8 PP	-1.6426	-1.7517 ^{c)}	0.1091	-1.6270	-1.7287 ^{c)}	0.1017	59.0	0.6

a) The results refer to the best Li_4 and Li_8 geometries obtained with the [6s1p/2s1p] AE basis set. The PP results have been obtained with a [4s1p/2s1p] basis set. The optimized Li-Li distance of Li_4 in PP (5.82 a.u.) is very close to the computed AE value for the same cluster (5.81 a.u.).

b) E_B singlet - E_B triplet.

c) MRD CI treatment with 7 M.

d) MRD CI treatment with 4 M.

e) MRD CI treatment with 1 M.

The computed correlation energies (E_{corr}), binding energies per atom (E_B/n) and singlet-triplet splittings of these two Li clusters are given in Table 2.1.4. The satisfactory agreement between PP and AE values indicates the possibility to extend the calculations on clusters containing a larger number of atoms without losing accuracy.

2.1.5 Na_4 -clusters

The rhombic form is predicted to be the most stable Na_4 cluster in the singlet state on the basis of AE MRD CI calculations (135) as well as pseudopotential calculations (171). The computed binding energies per atom for these two approaches are 10.82 and 7.88 kcal/mole, respectively, and they are well reproduced by our PP MRD CI calculations performed for the optimized all electron geometry (135) (see Table 2.1.5).

The PP calculations, in agreement with the AE results (135), predict the square form as the most stable triplet geometry. The singlet and the triplet energies for this cluster form lie very near each other and the sign and magnitude of this energy difference strongly depends on the AO basis set and on the kind of CI procedure employed. The agreement between PP results obtained here and by Flad et al. (171) is very good, the triplet binding energies per atom being 6.38 and 6.77 kcal/mole, respectively.

The combination of two Na_2 molecules in a so called T-form gives a cluster geometry whose stability is not too far from

Table 2.1.5 - Properties of Na_4 clusters^{a)}

	Method and basis set	Binding energy per atom (kcal/mole)		ΔE (singlet - triplet)	Ionization potential ^{b)} (eV)	
		singlet	triplet		singlet	triplet
rhombus	PP MRD CI [4s2p] ^{c)}	8.02	5.57	9.80	4.07	3.65
	AE MRD CI [7s3p] ^{d)}	10.82	—	—	4.17	—
planar square	PP MRD CI [4s2p] ^{c)}	5.68	6.38	-2.83	4.15	4.27
	AE MRD CI [7s3p] ^{d)}	8.16	9.52	-5.52	4.14	4.38
T-form	PP MRD CI [4s2p] ^{c)}	7.22	2.72	18.00	4.00	3.22
	AE MRD CI [7s3p] ^{d)}	10.01	—	—	—	—

a) The calculations have been performed for the following AE optimized geometries: rhombus: side length 6.58 bohr, angle 129° ; planar square: side length 6.2 bohr; T-form: $R_1 = 6.0$ bohr, $R_2 = 5.78$ bohr, $d = 6.7$ bohr (see fig. 2 for definitions).

b) Na_4^+ cations have been calculated with the SCF MOs of the Na_4 clusters. Experimental ionisation potential 4.27 ± 0.05 eV

c) 5M/1R treatment with $T = 0.4$ μ hartree.

d) 5M/1R treatment with $T = 0.4$ μ hartree. The CI procedure is applied only on 3s electrons.

that of the rhombic arrangement. We have performed an energy optimization at AE level for this T-form geometry employing the same AO basis set and the same 5M/1R treatment ($T=0$) in which only 3s electrons are correlated as in ref. (135). The minimal geometrical parameters derived from this calculation are $R_1 = 6.0$, $R_2 = 5.78$ and $d = 6.7$ a.u. (see Fig. 2.1.1 for definitions). These results confirm the prediction of Preuss et al. (128) who obtained an energy difference between the rhombic and the T-form of Na_4 in the singlet state of only 3.24 kcal/mole. Our PP MRD CI calculations predict this energy difference to be 3.20 kcal/mole.

The importance of the valence correlation is well shown in both AE and PP procedures by the prediction of very small or null stability of the sodium clusters at SCF level. It is interesting to compare the computed valence correlation energy for the rhombic form which in the PP and AE treatments amounts to -0.0531 and -0.0501 a.u., respectively. In spite of the fact that the two basis sets are not strictly comparable, this may be considered as a good test of the ability of the PP method to give accurate estimations of the correlation effects in alkali metal clusters.

Finally, we emphasize the satisfactory agreement between

PP ionization potential for the rhombic arrangement (4.07 eV) and the experimental value (4.27 eV) obtained by molecular beam techniques (21). The experimental decrease of the ionization potential on going from Na_2 to Na_4 (0.66 eV) is also well reproduced in the PP scheme (0.62 eV).

2.1.6 K_4 clusters

As pointed out in the section 2.1.3 the exclusion of the d polarization functions from the AO basis set gives results for the K_2 molecule which agree less with the experiment. For this reason some preliminary calculations have been performed with and without d-functions on ground states of rhombic, planar square, tetrahedron and T-form arrangements employing a limited CI procedure (1M/1R with $T=0.4$ microhartree). The results parallel those obtained for the K_2 molecule, that is, the inclusion of the d-functions yields smaller interatomic distances and slightly larger binding energies (Table 2.1.6) but the form of the wave function considered for the ground state and the qualitative ordering of the relative stabilities of the K_4 clusters are not affected.

More detailed calculations have been performed on K_4 clusters employing the basis set $|4s2p|$ (see Table 2.1.7). The importance of correlation energy in these potassium clusters is well demonstrated by the fact that all the geometrical arrangements considered are unstable at SCF level. The inclusion of correlation effects in a 6M/1R PP MRD CI pro-

Table 2.1.6 - Results for K_4 clusters with and without d-polarization functions

	Basis set $[4s2p1d]$		Basis set $[4s2p]$	
	side length (bohr)	binding energy per atom (kcal/mol)	side length (bohr)	binding energy per atom (kcal/mol)
rhombus	8.91	5.69	9.22	3.92
T-form	9.03 b)	5.07	9.36 b)	3.75
planar square	8.67	5.03	8.97	3.74
tetrahedron	8.91	4.09	9.37	2.59

a) 1M/1R treatment with $T = 0.4 \mu\text{hartree}$.

b) The result refers to the d distance

Table 2.1.7 - Properties of K_4 clusters for the singlet and triplet optimized geometries^{a)}

	Rhombus ^{b)}		T-form ^{c)}		Square planar		Tetrahedron	
	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet
side length (bohr)	9.27	9.32	$R_1 = 8.21$ $R_2 = 8.26$ $d = 9.32$	-	8.88	9.02	9.29	9.28
energy (au)								
$T = 0.4 \mu\text{hartree}$	-0.615925	-0.608205	-0.613983	-0.597944	-0.606440	-0.613418	-0.596681	-0.605820
extrapolated energy (au), $T \rightarrow 0$	-0.616154	-0.608455	-0.614365	-0.598277	-0.606523	-0.613612	-0.596840	-0.606112
estimated full CI energy (au)	-0.618721	-0.611906	-0.617569	-0.602182	-0.608513	-0.615158	-0.600493	-0.608255
correlation energy (au)	0.037548	0.029849	0.036584	0.020496	0.027226	0.034315	0.024253	0.033525
ionization potential (eV) ^{d)}	3.23	3.02	3.22	2.79	3.25	3.45	2.95	3.20
binding energy per atom (kcal/mol) ^{e)}	4.41	3.21	4.13	1.61	2.90	4.25	1.38	2.84
D_c into two K_2 ^{e)} (kcal/mol)	3.50	-1.58	2.38	-7.72	-2.54	2.87	-8.62	-2.80

a) 6M/1R treatment with $T = 0.4 \mu\text{hartree}$.

b) The rhombic angle was held fixed to the value of 127° .

c) The geometry optimization has been carried out only for the single ground state (see fig. 2 for definitions).

d) K_4^+ cations have been calculated with the SCF MOs of the K_4 clusters. Experimental ionization potential 3.6 eV

e) For determination of PP MRD CI binding energies per atom and dissociation energies the extrapolated energies are used.

cedure leads to a binding energy per atom of about 4 kcal/mole for the singlet state of rhombic and T-form and for the triplet state of square clusters.

An interesting result is that on going from Li to K the stabilization energy of the rhombic form decreases more rapidly than that of square and T-form. In addition we found that the triplet square and the singlet T-shaped structures are stable not only with respect to dissociation into four potassium atoms but also with respect to the dissociation into dimers.

The stabilities of the potassium clusters obtained with the PP MRD CI procedure are generally larger than those found by Stoll et al. (172) using the PP DF formalism. In fact they predict the T-form to be the only structure stable with respect to the dissociation into K_2 dimers the energy difference being 0.6 kcal/mole. Finally we report the geometrical parameters for the optimized T-form: $R_1 = 8.21$, $R_2 = 8.26$, $d = 9.32$ a.u..

2.1.7 Alkali metal clusters with five-fold symmetry

Ab initio studies of small alkali metal clusters have shown that the average coordination number of cluster atoms and the potential presence of the pseudo-Jahn-Teller or Jahn-Teller effect influence cluster stability very strongly. Since very compact clusters usually are also highly symmetrical, both tendencies can often work against each other. The distortion of the symmetry due to the presence of partially occupied one-electron levels in the leading electronic configuration (pseudo-Jahn-Teller effect) has been studied in detail for Li_4 . Here, the less compact rhombic geometry has a lower energy than the more compact tetrahedral and square arrangements. According to ab initio calculations, those Li clusters which can be considered as sections of the fcc crystal lattice have relatively very high binding energy per atom (BE/n) (168). On the other hand, ab initio studies indicate that Li_6 C_{5v} cluster (pentagonal pyramid) and Li_7 D_{5h} cluster (pentagonal bipyramid) are even more stable (162,168).

The recently published tentative interpretation of the ESR spectra of matrix isolated small alkali metal clusters (69,70) has motivated the investigation of clusters with an odd number of atoms as well. The Li_5 , Li_6 and Li_7 clusters which can be considered as steps in the pentagonal growth have been studied with the AE MRD CI method and Na_7 and K_7 clusters with the PP MRD CI approach. A preliminary investigation of the electronic structure of the anions Li_5^- , Li_6^- and Li_7^- illustrates the importance of the electron occupancy for the cluster stability.

The basis set used in the study of this class of Li clusters is the $|6s1p/2s1p|$ basis set described in Table 1 of ref. (137). With this basis set the stabilities of various Li clusters have been already compared (137,168). Consequently, this admittedly quite small basis set is suitable for a comparative study. The PP MRD CI investigation of Na_7 and K_7 is carried out with an AO basis set of $|4s1p/2s1p|$ character. The exponents and contraction coefficients are reported in Table 2.1.1. The exponents of the p-Gaussian functions (0.0951 and 0.0492 for Na and K, respectively) are determined by the optimization on diatomics Na_2

Table 2.1.8 - Binding energies and optimal geometries for pentagonal-type alkali metal clusters

Ground state	nM/w^a	Optimum geometry a.u. ^b		BE/n (kcal/mol)	Lowest triplet or quadruplet	nM/w^a	$E_B^1 - E_B^{1c}$ (eV)	$E_B^d - E_B^{1d}$ (eV)
		r_1	r_2					
$Li_5(D_{5h})$	$^2E_1'$	8M/0.87	5.78	...	10.3	$^4E_1'$	6M/0.87	...
$Li_6(C_{5v})$	1A_1	4M/0.85	5.91	5.84	14.1	$^3E_1'$	3M/0.83	1.1
$Li_7(D_{5h})$	$^2A_1'$	1M/0.82	5.94	5.92	14.8	$^4E_1'$	1M/0.82	...
$Na_3(D_{3h})$	$^2A_1'$	1M/0.84	6.97	7.00	8.2	$^4E_1'$	1M/0.85	...
$K_3(D_{3h})$	$^2A_1'$	1M/0.81	9.12	9.27	5.4	$^4E_1'$	1M/0.82	...

^a nM indicates the number of reference configurations from which all single and double excitations are generated. All configurations which contribute more than 1% to the CI expansion are chosen as reference configurations. $w = \sum c_i^2$ gives the total weight of the main configurations in the final CI wave function. Only the configurations causing an energy lowering larger than $5 \mu H$ are included in the final secular determinant.

^b r_1 is the distance between atoms in the pentagonal plane. r_2 is the distance between apical and in-plane atoms.

^cDifference in binding energy between singlet ground state and first triplet excited state

^dDifference in binding energy between doublet ground state and first quartet excited state.

and K_2 at equilibrium experimental distance.

The "pentagonal type" Li cluster shapes (pentagonal pyramid Li_6 and pentagonal bipyramid Li_7) with optimized interatomic distances are very stable (Tables 2.18 and 2.19). The values of BE/n are significantly although not much larger than those of the fcc-type Li clusters (planar Li_6 of D_{3h} and non-planar Li_7 of C_1 symmetry) (168).

Although the numerical values of BE/n depend, of course, on computational details, this result is significant and very convincing in its generality. For the pentagonal-type clusters, the binding energy per atom grows with increasing cluster size similarly as in the case of fcc-type clusters: BE/n is 10.3, 14.1 and 14.8 kcal/mole for Li_5 (D_{5h}), Li_6 (C_{5v}) and Li_7 (D_{5h}), respectively. BE/n is 12.8, 13.9 and 14.1 kcal/mole for Li_5 (C_{2v}), Li_6 (D_{3h}) and Li_7 (C_1), respectively (168).

The energy difference between lowest state of higher multiplicity and the ground state for pentagonal-type Li_6 and Li_7 clusters is clearly larger than for the corresponding fcc-type forms. On the contrary, it is much smaller in the more symmetrical Li_5 (D_{5h}) than in Li_5 (C_{2v}) (0.7 and 1.8 eV, respectively). The binding energies of pyramidal Li_6 and bipyramidal Li_7 vary only moderately with changes in interatomic distances as shown by a comparison of the BE/n values for energy optimized clusters

in Table 2.1.8 and the previously considered analogous clusters (168) with $r = 5.865$ a.u., the nearest neighbor distance in fcc Li crystal.

In general, the calculated interatomic distances in the pentagonal-type clusters are slightly larger than the average interatomic distances obtained in an optimization procedure for fcc-type clusters under the assumption of the equality of all interatomic distances. It is possible to recognize a general tendency for the bond lengths to elongate with the increasing coordination number ($r_1 = 5.91$ a.u. and $r_1 = 5.94$ a.u. for Li_6 (C_{5v}) and Li_7 (D_{5h}), respectively). Again, two trends influencing cluster stability seem to fight each other. The individual bonds become weaker with increasing coordination but the total number of bonds simultaneously grows and causes an increase of the cluster stability. Let us emphasize again at this point that the regularities and trends in the bond lengths rather than the detailed numerical results are significant because of the small extent of the basis set used.

The participation of p-polarization functions in leading configurations of the ground state wave function is a character-

Table 2.1.9 - Stability and pseudo-Jahn-Teller effect for pentagonal-type lithium clusters

Cluster and geometry					
	Li_5 (D_{5h})	Li_5 (C_{2v})	Li_5 (C_{2v})	Li_6 (C_{5v})	Li_7 (D_{5h})
Neutral forms ^a					
Ground state	${}^2E'_1$	2A_1	2A_1	1A_1	${}^2A_1''$
E_{SCF} (a.u.)	-36.8986	-36.9119	-36.9316	-44.3169	-51.7181
E_{CI} (a.u.)	-36.9275	-36.9789	-36.9927	-44.4031	-51.8122
BE/n (CI)	10.3	11.1	12.8	14.1	14.8
(kcal/mol)					
Anionic forms ^b					
Ground state	${}^1A_1'$	1A_1	1A_1	2A_1	${}^1A_1'$
E_{SCF} (a.u.)	-36.9144	-36.9158	-36.9187	-44.3011	-51.7012
E_{CI} (a.u.)	-37.0041	-37.0047	-37.0055	-44.3942	-51.8136
BE/n (CI) ^c	14.3	14.3	14.4	13.1	15.0
(kcal/mol)					
BE/n (CI) ^d	15.5	15.5	15.6	14.2	15.8
(kcal/mol)					

^aFor details of the MRD CI treatment see Table I.

^bThe details of the MRD CI treatment are: Li , $6M/0.85$; Li , $1M/0.81$; Li , $1M/0.81$.

^cThe dissociation energy is computed with respect to n neutral Li atoms.

^dThe dissociation energy is computed with respect to $(n-1)$ neutral Li atoms plus Li^- .

istic property of the Li clusters. The role of these orbitals is reminiscent of the concept of Slater's metallic orbitals. The p-polarization functions are very often decisive for the determination of the optimal cluster shape.

In the ${}^2A_2''$ ground state for the Li_7 bipyramid the natural orbital with occupation number approximately equal to one is practically identical with the a_2'' SCF molecular orbital. This orbital exhibits large coefficients of opposite signs of the s basis functions at apical atoms and quite significant coefficients at the p functions located at the centers in the plane of the pentagon. In both Li_7 and Li_6 , the Mulliken population analysis of all three p orbitals at the apical centers is larger than the population of the p orbitals in the plane of the pentagon.

As the highest occupied e_1' orbital of the anion Li_5^- (D_{5h}) cluster is slightly bonding and fully occupied the Li_5^- (D_{5h}) does not show a pseudo-Jahn-Teller effect. The symmetrical form is therefore stable and the deformation to Li_5^- (C_{2v}) is not energetically favoured. At least when electron correlation is taken into account, the anions Li_5^- and Li_7^- are more stable than the corresponding neutral species. The importance of the electron correlation is apparent from the fact that the SCF energy of the planar Li_5^- is quite insensitive to the geometrical changes. The odd-electron system Li_6^- (C_{5v}) has only slightly higher total energy than the neutral Li_6 (C_{5v}).

In this connection it is worth noting that both rhombic Li_4^- and tetrahedral Li_4^- anions are more stable than the corresponding neutral species according to the MRD CI calculations with the same AO basis set. The difference between tetrahedral Li_4^- and the very unstable tetrahedral Li_4 is 0.019 a.u., whereas the total energy of the rhombic Li_4^- is only 0.004 a.u. lower than that of the neutral rhombic Li_4 .

The relative stability of the ions would be, of course, only more pronounced if a set of basis functions appropriate for the description of the anions were used. Evidently, the AO basis set chosen for the neutral species is biased strongly against the anions. Moreover, the geometries have been optimized for the neutral clusters.

Table 2.1.10 - Electron distribution and ESR hyperfine coupling constants in pentagonal-type alkali metal clusters

		Unpaired electron distribution		Total electron population	Hyperfine coupling constants		
		MO ^a	NO ^a	NO	MO ^b	NO ^b	Exp
Li ₅	s	0.1594	0.1630	2.8247	8.6	8.8	...
	p	0.0406	0.0370	0.1753			
	apical s	...	...	2.3958	...	...	...
	atom p	...	...	0.4200			
Li ₆	basal s	...	...	2.8870	...	...	...
	atoms p	...	...	0.1498			
	apical s	0.3550	0.3466	2.6158	19.2	18.7	13.9 ^c
	atoms p	0.0147	0.0124	0.3259			
Li ₇	basal s	0.0000	0.0000	2.8259	...	...	0.8 ^c
	atoms p	0.0521	0.0517	0.1974			
	apical s	0.4525	0.4128	0.7318	143.0	140.0	117 ^d
	atoms p	0.0030	0.0020	0.2225			
Na ₇	basal s	0.0000	0.0000	0.9445	...	...	6.5 ^d
	atoms p	0.0178	0.0186	0.0738			
	apical s	0.4469	0.4364	0.7230	36.8	36.0	30.6 ^d
	atoms p	0.0041	0.0028	0.1520			
K ₇	basal s	0.0000	0.0000	0.9453	...	...	1.8 ^d
	atoms p	0.0196	0.0202	0.1047			

^a Electron distribution computed on the basis of molecular orbitals (MO) and natural orbitals (NO).

^b The following hyperfine atomic constants have been used: $a(^6\text{Li}) = 54.29 \text{ G}$; $a(^{23}\text{Na}) = 316.09 \text{ G}$; $a(^{39}\text{K}) = 82.38 \text{ G}$ (183).

^c From Ref. 69

^d From Ref. 70

Thompson et al. (70) have studied sodium and potassium heptamers and they have correctly recognized the plausibility of the pentagonal bipyramid shape for Na₇ and K₇. Therefore, we have extended our investigation to these heavier alkali metal heptamers using the PP MRD CI technique. The optimized geometries for Na₇ (D_{5h}) and K₇ (D_{5h}) are given in Table 2.1.8. The similarities among the alkali heptamers are obvious in spite of the different methods of calculation used for Li₇ (AE MRD CI), Na₇ and K₇ (PP MRD CI).

For example, note the similar participation of p functions at apical and basal atoms in Li₇, Na₇ and K₇. The degree of s-p hybridization is far largest in the case of Li₇. The high con-

tribution of the Li p orbitals is reflected in the relatively small s character of the Fermi electron as shown by the values of the ESR hyperfine coupling constants. The computed values of Table 2.1.10 are in qualitative agreement with the experimental ones, despite the limitation of the basis set and the fact that in Na_7 and K_7 only the outermost s functions are considered.

The Jahn-Teller or the pseudo-Jahn-Teller effect together with the tendency towards the most compact geometrical arrangement possible are decisive in the determination of the geometry of alkali metal clusters. The reasons for the relatively strong binding in pentagonal-type Li clusters can be attributed to two features: the clusters Li_6 (C_{5v}) and Li_7 (D_{5h}) are very compact; simultaneously all degenerate one-electron levels in the leading configuration of the CI ground state wave function $(a_1)^2(e_1)^4$ and $(a_1')^2(e_1')^4(a_2'')^1$, respectively, are fully occupied. Consequently, no Jahn-Teller effect or pseudo-Jahn-Teller effect can distort these cluster symmetries and, moreover, the ground states have the minimal spin multiplicity. The opposite situation is found in the case of Li_5 (D_{5h}) with a ground state configuration $(a_1')^2(e_1')^3$. The Jahn-Teller effect leads here to a symmetry lowering resulting in a C_{2v} geometry (Table 2.1.9). The analogy between the distortion of Li_5 (D_{5h}) to Li_5 (C_{2v}) and the relaxation of tetrahedral or square to rhombic Li_4 due to the pseudo-Jahn-Teller effect is evident.

The present MRD CI investigation predicts a slightly higher stability for the pentagonal bipyramid Li_7 compared to the Li_7 structure which is a part of the fcc crystal lattice. The pentagonal bipyramid exhibits a group of two equivalent and another group of five equivalent centers in agreement with the tentative analysis of the ESR measurements (69,70). The relatively important participation of the p orbitals which increases with cluster size, the similarity between the Li, Na and K clusters, and the especially high degree of s-p hybridization for lithium clusters are features in which the theory and the analysis of the ESR experiments agree completely.

2.2 ALKALINE-EARTH METAL CLUSTERS^{*}

2.2.1 Introduction

Among alkaline-earth metal clusters Be clusters are the most intensively studied for the obvious reason that the number of electrons to be treated at all electron level is relatively small. Moreover, Be clusters have been the subject of many ab initio studies because the assumption that a cluster of Be atoms has a closed shell ground state greatly simplifies the theoretical treatment. However, as we shall consider in the next sections, not always this assumption corresponds to a real physical situation.

Starting from the basic hypothesis that Be clusters have a singlet closed shell ground state, Bauschlicher et al. (188) have studied in 1975 the electronic structure of Be aggregates containing up to 10 atoms at all electron SCF level adopting a minimal basis set. All the structures considered (188) were taken as sections of the hcp crystal lattice of metallic Be and were used to model the H chemisorption on a metallic surface. The attention in this work was mainly concentrated on the chemisorption problem, but some basic features of this class of clusters were clearly established. In particular, Be 2p functions were found to play a crucial role in the electronic structure of the cluster.

A very interesting problem is the difference in stability between Be₂, which is a virtually non bonded molecule, and tetrahedral Be₄ which, on the contrary, displays a considerable stability. The nature of the bonding in this latter cluster was studied at SCF level by Brewington et al. (189) and the stability of this Be tetramer was correctly attributed to the strong sp hybridization. Using the CEPA method, Dykstra et al. (190) have found that the correlation energy in Be₄ tetrahedron is relatively small.

^{*} The present chapter has been partly published in the papers /2/, /3/, and /7/ of the list of p. 201.

Jordan and Simons (191,192) have performed SCF calculations on neutral and anionic forms of Be_2 , Be_3 and Be_4 and of Mg_4 (193). An electron affinity of 1 eV was found for Be_4^- . Moreover, Be_2^- and Be_3^- were found to be slightly stable, while the corresponding neutral clusters do not display appreciable stability. A small stability was found also for the Mg_4^- cluster (193).

When a metal cluster is formed one can express the interaction energy as sum of n-body interaction energies, e.g., in a tetrahedral Be_4 system six 2-body interactions plus four 3-body interactions and a 4-body interaction. Kolos and Novaro (194,195) have discussed non-additive effects in these interactions using SCF calculations of total interaction energies for Be_3 , Be_4 and Be_5 . They found that 2-body and 4-body terms give a repulsive contribution to the interaction energy, whereas the 3-body terms are attractive. A similar investigation was carried out by Daudey et al. (196) on Mg clusters. However, in contrast to tetrahedral Be_4 , tetrahedral Mg_4 was found to be non bonded. Basis sets including only p-polarization functions were used in these studies.

A detailed study of small size Be clusters was done by Whiteside et al. (197) using restricted Hartree-Fock calculations for closed shell singlets and spin-unrestricted Hartree-Fock for higher multiplicities. The correlation effects were considered by means of the Møller-Plesset perturbation theory. They have a dramatic effect on the relative energies of the several structures examined. Furthermore, the influence of d-functions on the correlation energy is that to produce an increase of the binding energy of the cluster.

In the pseudopotential study of Stoll et al. (172) the binding energies of small Be, Mg and Ca clusters were found to be very small or null with the exceptions of tetrahedral Be_4 and Ca_4 and bipyramidal trigonal Be_5 .

The electronic structure of tetrahedral Mg_4 was considered by Chiles et al. (198) adopting a large basis set including d-functions. Correlated wave functions were obtained with the

self-consistent-electron-pairs (SCEP) method. A small stability for this Mg tetramer was observed (198). The nature of the bond in Mg_4 and Ca_4 clusters and the role of d-functions on the degree of s-p hybridization are the subject of a recent work of Bauschlicher et al. (199). Using a minimal basis set the SCF wave function of Be_{13} and Mg_{13} was determined. Taking the central atom as a model for a bulk atom it was possible to relate the degree of hybridization in the metal to the heats of sublimation (199).

Beryllium clusters containing a larger number of atoms have been examined by Bauschlicher, Bagus, Schaefer III and co-workers (200-204). Clusters sections of the hcp Be crystal lattice were considered as a substrate for H chemisorption. The largest cluster considered is a Be_{36} cluster studied at SCF level with a minimal basis set (204). A number of properties including singlet-triplet energy separation, ionization potential and binding energy were computed. A convergence of some properties to the values typical for the bulk metal was found. For instance, the ionization potential (IP) computed as the energy difference between the neutral and the cationic species decreases from 8.44 eV at Be to 4.71 eV at Be_{22} . This latter value is quite close to the work function of metallic beryllium. The binding energy per atom was found to grow with the increasing cluster size but the value computed for the largest Be_{36} cluster, 23.0 kcal/mole, is still far from the cohesive energy of Be crystal (78 kcal/mole).

The nature of the charge distribution in Be clusters was also examined by considering the Mulliken atomic populations. A shift of charge from the "surface" layers to the middle layer was found in the largest cluster. Moreover, it was found that the degree of hybridization strongly depends on the number of neighboring atoms and that (while the 2s population is inversely proportional to the number of near neighbors of the atom) the 2p population increases with the number of neighbors (204).

In the following are discussed some theoretical results on the electronic structure of the alkaline-earth metal clusters

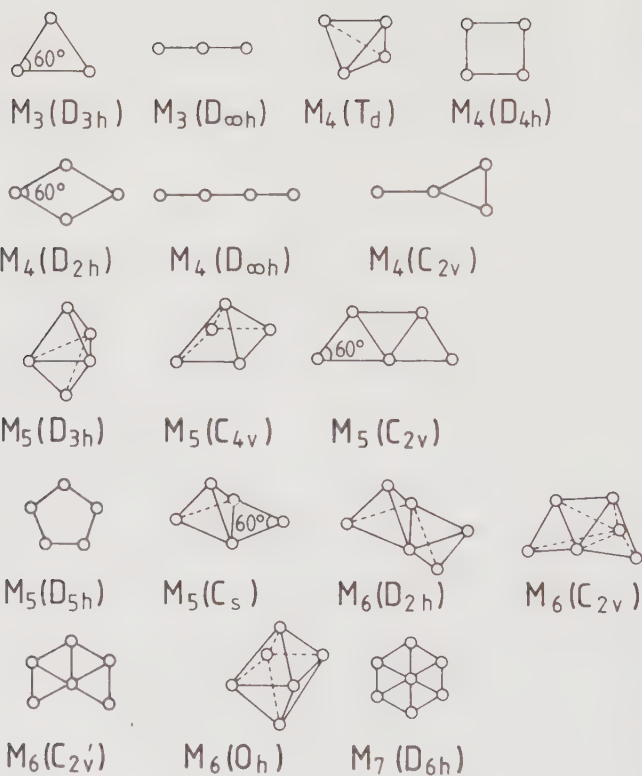


Fig. 2.2.1 - Structures of the investigated alkaline-earth metal clusters ($M = \text{Be}, \text{Mg}, \text{Ca}$).

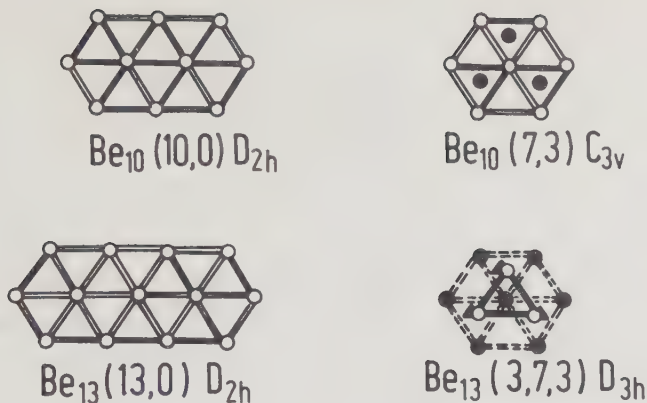


Fig. 2.2.2 - Structures of the investigated Be_n clusters ($n = 7, 10, 13$); (o) first layer atoms, (o) second layer atoms, (▲) third layer atoms. The geometrical arrangement of the Be₇(7,0) (D_{6h}) cluster is shown in Fig. 2.2.1.

Be₁, Mg_m and Ca_n ($1 \leq 13$, m and $n \leq 5$); see Fig. 2.2.1 and 2.2.2 for the geometrical definitions). Being characterized by a closed shell electronic configuration, a system of two alkaline-earth atoms is experimentally practically not stable, unlike the bulk solid. Thus one question of interest for this group of clusters is related to the change occurring as the cluster grows, gradually forming a metallic crystal. In this respect the properties of alkaline-earth metal clusters are very different from those of alkali clusters. Another point requiring investigation concerns the possibility to extrapolate the results here obtained for the Be clusters not only to the other elements of Group IIa, Mg, Ca, Sr and Ba, but in general to all clusters of atoms with the ns^2 electronic configuration, e.g. Zn, Cd, Hg.

The question of the optimum geometry of these small clusters has been investigated and will be discussed in the next sections. The splitting between singlet and triplet states is

difficult to be rationalized without a systematic analysis. Therefore we have considered the energy difference between the two lowest singlet and triplet states for the optimal geometry of the singlet state or for the distance present in the bulk metal (about 4.2 a.u.). The study of Whiteside et al. (197) has shown that the restricted and unrestricted Hartree-Fock approaches can give for some (mainly linear) cluster-geometries uncorrect results on the stability and spin multiplicity.

For these reasons a systematic investigation with a method allowing in principle the description of the electron correlation has been carried out. Finally, the indicative appearance of some properties of the bulk metal with the increasing cluster size has been analyzed.

2.2.2 Computational details and basis set specification

The theoretical approach chosen for this series of calculations is the PP MRD CI method previously described (see Section 1.2). Few all electron calculations have been carried out in special cases where the PP method seemingly did not agree with some published results. The use of a PP method in the study of Be clusters can look unjustified because of the relatively small saving of computation time. However, the exclusion of the core electrons from the calculation facilitates the description of the chemical properties due to the valence orbitals and permits extension of the investigation to systems containing a larger number of atoms. A thorough and systematic investigation of the general impact of the pseudopotential approach upon the physical and chemical properties of clusters is a necessary prerequisite for the practical introduction of further simplifications (e.g. concerning the AO basis set). Moreover, the detailed investigation of clusters of the heavier Mg and Ca atoms is not practicable by means of the usual all electron calculations.

For the calculations on Be, Mg and Ca we have adopted an uncontracted PP basis set consisting of four Gaussian functions optimized at atomic level (116). The exponents and contraction

Table 2.2.1 - Pseudopotential basis sets for Be, Mg and Ca

	Orbital	Exponent
Be a)	s	18.0499
	s	2.21327
	s	0.152533
	s	0.052965
	p	0.35
	p	0.07
	d	0.05
Mg	s	4.27430
	s	0.753377
	s	0.101525
	s	0.037562
	p	0.50
	p	0.10
	d	0.40
Ca	s	1.07496
	s	0.329981
	s	0.062666
	s	0.025244
	p	0.40
	p	0.05
	d	0.40

a) A second set of p polarization functions [4p/2p] adopted for the calculation of some Be clusters, was taken from ref. 205. For the largest cluster considered, Be₇, the two inner s functions have been contracted with the following coefficients: -0.008533 and -0.054339.

coefficients of these basis sets are given in Table 2.2.1. However, the description of the bonding in alkaline-earth compounds dramatically depends on the choice of p and, especially for Mg and Ca, of the d-polarization functions. All p and d exponents were roughly optimized at molecular level for the diatomic molecules (Table 2.2.1). However, the results of our investigation show that the optimization of the d-exponent in the case of Mg and Ca has to be done on larger clusters because in these systems a new kind of chemical bond occurs (see Sections 2.2.6 and 2.2.7).

From the theoretical point of view, the combination of 2 atoms with a ns^2 atomic ground configuration gives rise to a molecular configuration with the same number of bonding and antibonding orbitals so that the description of the very weak interaction predicted on this basis requires a great accuracy.

One very important effect on the relative stability of the clusters is the appearance of the correlation size effects. While at atomic level the singlet ground state main configuration accounts for more than 90 per cent of the CI wave function, for the M_n clusters ($M = \text{Be}, \text{Mg}, \text{Ca}$) this contribution becomes smaller and smaller and, at the same time, we have an increasing number of configurations giving small contributions to the final CI wave function. As an example we report the composition of the CI wave function for Mg , Mg_2 , triangular Mg_3 , tetrahedral Mg_4 and bipyramidal trigonal Mg_5 clusters.

For sake of brevity we refer to the contribution of the singlet ground state main configuration as MC and to the sum of all other n configuration contributions greater than 0.2 per cent as SC (n). With this in mind we observe that in the case of the atom MC corresponds to the 92.7 per cent while SC (4) represents the 7.17 per cent of the CI wave function; this means that with 5 main configurations it is possible to describe 99.9 per cent of the atomic CI wave function. For the Mg_2 molecule the MC value drops to 0.879 and SC (17) is equal to 0.115; for triangular Mg_3 we have $\text{MC} = 0.846$, $\text{SC} (20) = 0.077$; for tetrahedral Mg_4 $\text{MC} = 0.820$, $\text{SC} (13) = 0.034$; finally, for the bipyramidal trigonal Mg_5 cluster the values are $\text{MC} = 0.799$ and $\text{SC} (12) = 0.031$.

In other words, even a great number of main configurations cannot give, for the larger clusters, a description better than the 83 per cent of the CI wave function. This effect is strictly connected with the closed shell nature of these alkaline-earth clusters, but can be encountered also in other cases. Because of the different quality of the atomic and molecular CI description, the total energy of a M_n cluster can be compared with the energy of n separated atoms only at the Hartree-Fock level.

Also, because only two valence electrons are present in the Group IIa metal atoms, all possible single and double excitations give the full CI description of the atomic electronic structure. On the contrary, the full CI energy at molecu-

Table 2.2.2 - Computational details of the CI calculations for medium-size Be clusters

	Be ₇ (7,0)		Be ₁₀ (10,0)		Be ₁₀ (7,3)		Be ₁₃ (13,0)		Be ₁₃ (3,7,3)	
	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet	singlet	triplet
nM/nR ^{a)}	2M/2R	1M/1R	3M/3R	1M/1R	1M/1R	1M/1R	2M/2R	1M/1R	1M/1R	1M/1R
number of generated configurations	5748	11069	35528	46847	40421	158548	68418	144243	58505	234937
selection threshold T (μ hartree)	10	10	70	25	30	20	60	30	30	30
number of selected configurations	3545	4108	4514	4030	3412	4314	4536	2921	4795	4410
$\sum_i c_i^2$ ^{b)}	0.78	0.81	0.82	0.79	0.81	0.81	0.80	0.85	0.80	0.82

^{a)} nM : number of leading configurations in MRD CI procedure; nR : number of roots searched in the final diagonalization of the CI matrix.

^{b)} The total weight of leading configurations in the correlated wavefunction.

lar level can only be estimated by means of the already mentioned Davidson formula (Section 1.2.3). These difficulties in the CI computation of the dissociation energy can be partly eluded considering as a reference point the total energy of the cluster whose atoms are placed at infinite distance (supermolecule); in this case the CI description of the cluster in its equilibrium geometry and that of the supermolecule are of similar quality. Therefore, the relative energies are comparable.

However, it should be noted that all these effects are actually quite small. They are not decisive when the order of magnitude of the stabilities is of some tens of kcal/mole, but they become non-negligible when the energies at stake are of few tenths of kcal, as in the case of some Mg clusters.

For the investigation of larger Be_n aggregates ($n = 7, 10, 13$) the four *s* Gaussian type orbitals of Table 2.2.1 have been contracted to two *s* functions for the description of the valence region of the Be atom. Four *p*-polarization functions from ref. (205) have been contracted to one *p* function. The final $|4s4p/2s1p|$ PP basis set has shown a qualitative agreement with the results obtained with the larger $|4s4p/4s2p|$

PP basis set for Be_7 . The details of the CI calculations carried out on larger Be_n clusters are given in Table 2.2.2. The number of selected configurations ranges from 3000 to 4800 while the generated CI space is much larger (up to 234 000).

2.2.3 Alkaline-earth metal dimers

The computed Hartree-Fock potential energy curves agree with the prediction of the simple qualitative MO theory that the $^1\Sigma_g$ ground states of Be_2 , Mg_2 and Ca_2 have repulsive character. The absence of a minimum in the SCF curve indicates that the employed basis set is flexible enough in order to avoid basis set superposition errors.

This result agrees with all other SCF studies on the electronic structure of Be_2 (199,206), Mg_2 (207,208) and Ca_2 (172) where sufficiently complete basis sets are used. The SCF and

Table 2.2.3 - Results for alkaline-earth dimers^{a)}

	R^b	E_{SCF}	$E_{\text{CI}}(\text{BE})$	$E_{\text{full CI}}(\text{BE})$	$\Sigma \epsilon_i^2$
[4s2p]					
Be_2	100.0	-1.9332	-2.0127	-2.0237	0.86
Be_2	9.27	-1.9330	-2.0130 (0.14)	-2.0240 (0.17)	0.86
$\text{Be} + \text{Be}$	-	-1.9332	-2.0191	-	0.91
Mg_2	100.0	-1.5687	-1.6288	-1.6361	0.88
Mg_2	10.7	-1.5684	-1.6289 (0.07)	-1.6362 (0.09)	0.88
$\text{Mg} + \text{Mg}$	-	-1.5687	-1.6329	-	0.93
Ca_2	100.0	-1.2104	-1.2574	-1.2640	0.86
Ca_2	12.3	-1.2103	-1.2577 (0.16)	-1.2643 (0.17)	0.86
$\text{Ca} + \text{Ca}$	-	-1.2104	-1.2613	-	0.91
[4s2p1d]					
Be_2	100.0	-1.9332	-2.0131	-2.0241	0.86
Be_2	8.31	-1.9327	-2.0139 (0.46)	-2.0250 (0.57)	0.86
$\text{Be} + \text{Be}$	-	-1.9332	-2.0195	-	0.91
Mg_2	100.0	-1.5687	-1.6296	-1.6369	0.88
Mg_2	9.5	-1.5682	-1.6230 (0.24)	-1.6374 (0.32)	0.88
$\text{Mg} + \text{Mg}$	-	-1.5687	-1.6337	-	0.93
Ca_2	100.0	-1.2104	-1.2599	-1.2663	0.87
Ca_2	10.0	-1.2098	-1.2608 (0.55)	-1.2674 (0.67)	0.87
$\text{Ca} + \text{Ca}$	-	-1.2104	-1.2636	-	0.92

a) All values are in au except the binding energies (BE) which are in kcal/mole.

b) The optimized distance refers to the CI calculation.

MRD CI results obtained with the two $|4s2p|$ and $|4s2p1d|$ basis sets are summarized in Table 2.2.3. At the highest level of the method used, full CI treatment with the larger basis set, the values of the binding energies (in kcal/mole) and of the equilibrium bond distances (in a.u.) are 0.57 and 8.1 for Be_2 , 0.32 and 9.4 for Mg_2 , 0.67 and 9.6 for Ca_2 , respectively. The large differences in the equilibrium geometries obtained with the two basis sets (see Table 2.2.3) indicate that a much larger basis is required to obtain more realistic results.

The effect of the inclusion of d-functions is more pronounced in the case of Mg_2 and Ca_2 , as may be expected. These results are parallel to those obtained by Stoll et al. (172) with a different PP method, but are quite far from the experimental dissociation energies of 1.2 kcal/mole (Mg_2) and 3.0 kcal/mole (Ca_2) as well as from the experimental bond lengths of 7.35 a.u. (Mg_2) and 8.09 a.u. (Ca_2) (209).

The differences between the computed and the experimental values can be attributed in part to the relative poorness of the basis set and in part to the pseudopotential method itself. The exclusion of the innershell correlation is also questionable in the case of alkaline-earth dimers. It is important to note, however, that also the experimental measurements are not always in agreement, and, for the Ca_2 molecule, where the band spectroscopic analysis predicts a binding energy of 3.0 kcal/mole (210), the laser photoluminescence experiments lead to the conclusion that the $^1\Sigma_g$ ground state is not bonded at all (211). The small binding energies and quite large equilibrium bond distances experimentally found for Mg and Ca dimers are in agreement with a nominal zero bond order.

Following some authors (191) it is logical to expect a similar shallow minimum also for the $^1\Sigma_g$ state of Be_2 even though experimental evidence is not available. Our present results and most of the reported calculations (172,191,197,212,213) support this hypothesis in contrast with the findings of Liu and McLean et al. (214,215) who, on the basis of the interacting correlated fragment method, predict a dissociation energy of 2.3 kcal/

mole and an equilibrium distance of 4.7 a.u. (214). Recently, Chiles and Dykstra (216,217) have pointed out the problematic nature of the Be_2 potential energy curve, showing how different kind of theories, in particular non-variational approaches, can produce very different results (216).

A highly accurate study of the bonding in Group IIa diatomic molecules is not the purpose of this study and this discussion of our results is merely intended to show the method and the basis set used.

2.2.4 Small size Be_n clusters ($n = 3-6$)

2.2.4.1 Be_3

The next smallest cluster after diatomic beryllium, linear and triangular Be_3 , do not appear to be appreciably bound if d-functions are not included in the AO basis set (172,191), and the very small stability has been attributed purely to correlation effects (172), as confirmed by the results of Table 2.2.4.

Table 2.2.4 - Electronic properties of Be clusters^{a)}

	Side bond length (Cl)	E_{SCF}/Be singlet	E_{SCF} triplet ^{b)}	E_{Cl}/Be singlet	$E_{\text{full Cl}}/\text{Be}$ singlet	IP
$\text{Be}_3(\text{D}_{\infty h})$	9.1	-2.8995/- ^{c)}	-2.9756 ^{d)}	-3.0115/0.3	-3.0304/0.4	8.06 ^{e)}
$\text{Be}_3(\text{D}_{3h})$	9.2	-2.8984/- ^{c)}	-	-3.0120/0.7	-3.0305/0.5	8.1 ^{e)}
$\text{Be}_4(\text{T}_d)$ ^{f)}	4.0 ^{g)}	-3.9223/35.0	-	-4.0721/34.5	-	7.47 ^{e)}
$\text{Be}_4(\text{T}_d)$	4.2	-3.8848/11.5	-3.8445	-4.0336/16.7	-4.0631/17.9	7.68
$\text{Be}_4(\text{D}_{2h})$	9.7	-3.8661/- ^{c)}	-3.7936	-4.0078/0.5	-4.0356/0.7	8.67
$\text{Be}_4(\text{D}_{4h})$	9.9	-3.8662/- ^{c)}	-3.8365 ^{h)}	-4.0077/0.4	-4.0354/0.5	8.66
$\text{Be}_5(\text{D}_{3h})$	4.1	-4.8434/10.0	-4.8154	-5.0405/24.8	-5.0736/26.0	6.41
$\text{Be}_5(\text{C}_{4v})$	4.2	-4.8380/3.1	-	-5.0056/3.0	-5.0397/4.7	5.71 ^{e)}
$\text{Be}_5(\text{C}_s)$	4.1 ^{g)}	-4.8315/-1.0	-	-5.0218/13.1	-5.0556/14.7	5.87 ^{e)}
$\text{Be}_5(\text{C}_{2v})$	9.4	-4.8320/- ^{c)}	-4.7826 ⁱ⁾	-5.0024/0.9	-5.0387/4.1	8.12 ^{e)}
$\text{Be}_5(\text{D}_{5h})$	4.2	-4.8759/26.9	-	-5.0200/11.9	-5.0474/9.6	6.38 ^{e)}
$\text{Be}_6(\text{D}_{2h})$ ^{f)}	3.8	-5.8728/45.9	-5.8569/35.9	-6.0831/54.5	-6.1190/55.1	6.18 ^{e)}
$\text{Be}_6(\text{C}_{2v})$ ^{f)}	4.0	-5.8726/45.7	-	-6.0785/51.6	-6.1135/51.5	5.97 ^{e)}
$\text{Be}_6(\text{O}_h)$ ^{f)}	4.0 ^{g)}	-5.8606/38.3	-	-6.0676/44.8	-6.1023/44.5	5.92 ^{e)}
$\text{Be}_6(\text{C}_{2v})$ ^{f)}	4.0 ^{g)}	-5.8527/33.3	-5.8430/27.2	-6.0542/36.3	-6.0910/37.5	6.00 ^{e)}
$\text{Be}_7(\text{D}_{6h})$ ^{j)}	4.0 ^{g)}	-6.8479/51.2	-6.8927/79.4 ^{k)}	-7.1122/82.1	-7.1664/83.0	5.83 ^{e)}

^{a)} If not explicitly mentioned the results refer to the [4s2p] basis set. All values are in au except the binding energies (BE) and the ionization potentials (IP) which are in kcal/mole and in eV respectively.

^{b)} The triplet SCF energies refer to the optimum singlet geometry.

^{c)} The Hartree-Fock curve is always repulsive.

^{d)} This energy refers to the optimized Cl triplet geometry of 4.0 au. The relative Cl energy is -2.9756 au.

^{e)} Koopman's theorem. ^{f)} The [4s4p/4s2p] basis set was adopted. ^{g)} Distance not optimized.

^{h)} This energy refers to the distance of 4.0 au. The relative singlet energy is -3.8508.

ⁱ⁾ This energy refers to the distance of 4.2 au. The relative singlet energy is -4.7978.

^{j)} The [4s4p/3s2p] basis set was adopted.

^{k)} For this distance the triplet Cl energy is -6.8927 au and the Cl binding energy 84.2 kcal/mole.

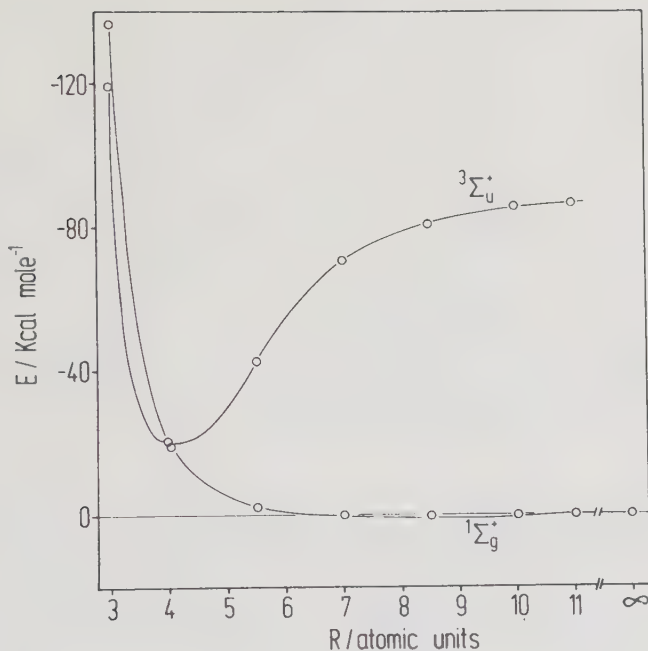


Fig. 2.2.3 - CI potential energy curves for the lowest $1\Sigma_g^+$ and $3\Sigma_u^+$ states of linear Be_3 .

On the contrary, a stability of 6 kcal/mole has been predicted for the triangular Be_3 using a basis set including d-polarization functions (197). The present calculations performed with the $|4s2p1d|$ basis set for the distance 4.2 a.u. indicate a dissociation energy of 7.1 kcal/mole for this cluster.

In the same work (197) the $3\Sigma_u^+$ state of linear Be_3 has been found to be lower in energy than the $1\Sigma_g^+$ one, with a stability of about 30 kcal/mole measured with respect to the dissociated three Be atoms. In this case, however, the Møller-Plesset perturbation estimate of correlation corrections yields the values 6.8 and -9.4 kcal/mole for the dissociation energy, using basis sets with and without d-functions, respectively (197). This result is quite surprising in view of the previous findings on

Be_2 and linear Be_3 (191), for which a singlet ground state was always predicted. Therefore we have carried out the study of the biradical character of linear Be_3 .

Potential energy curves obtained with the $|4s2p|$ basis set for the two $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states of linear Be_3 closely resemble those of diatomic Be and exhibit a slightly bonding $^1\Sigma_g^+$ state. The curves for the singlet and triplet states cross at interatomic distance R around 4 a.u. so that for smaller R the triplet state has lower energy than singlet (Fig. 2.2.3). The inclusion of d-polarization functions in the basis set, however, reverses the situation. The calculation performed with the $|4s2p1d|$ basis set gives in fact the minimum of the $^3\Sigma_u^+$ state about 8 kcal/mole below the dissociation limit.

2.2.4.2 Be_4

After the first study of Bauschlicher et al. (188) on a nearly tetrahedral Be_4 several different theoretical investigations of this highly symmetrical structure have been published. The effect of correlation was considered by Dykstra et al. (190) and does not seem to alter greatly the Hartree-Fock results.

The predicted stability for this geometrical arrangement lies between 30 and 40 kcal/mole (172,191,193,197) and the effect of the inclusion of d-functions in the basis set increases this value by about 50 per cent (181).

Three different basis sets have been adopted in our PP calculations. The first one is the already mentioned $|4s2p|$ basis set which gives a potential energy curve characterized by a pronounced minimum at a distance of 4.17 a.u. and by a second shallow minimum at larger nuclear separation (Fig. 2.2.4a). The computed stabilities of 11.5 (SCF) and 16.7 (CI) kcal/mole (Table 2.2.4) are markedly different from most of the reported dissociation energies.

This result is not due to the use of the PP method: the all electron calculation, performed with a $|9s2p/5s2p|$ basis set (this basis set has been built up using the GTO basis set

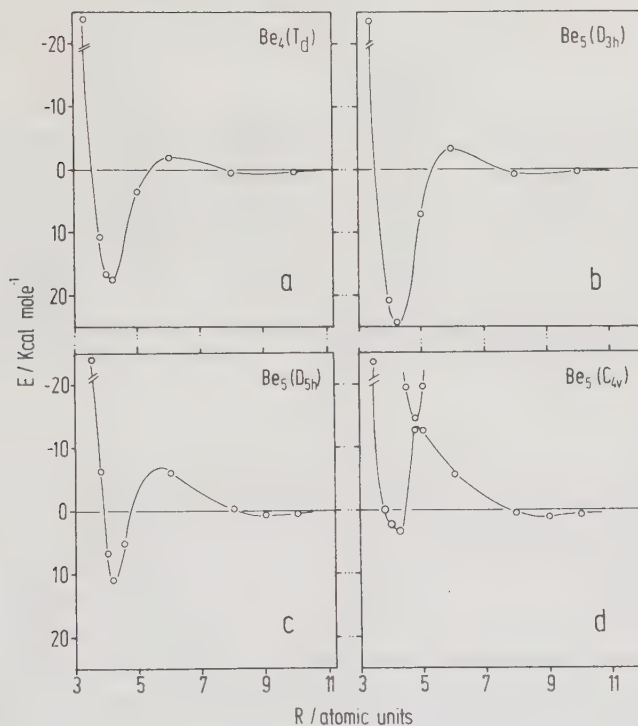


Fig. 2.2.4 - CI potential energy curves for the ground states of Be_4 (T_d) (a), Be_5 (D_{3h}) (b), Be_5 (D_{5h}) (c) and Be_5 (C_{4v}) (d) clusters. All the curves are characterized by a double minimum nature resulting from an increased participation of p atomic orbitals in the bond at shorter distances.

of van Duijneveldt (F. van Duijneveldt, I.B.M. Techn. Report R.J. 945, Dec. 1971) adopted in the Dykstra's calculation (190) and adding the same two uncontracted Gaussian p-polarization functions of the PP calculation) gives in fact a binding energy of 10.0 and 15.7 kcal/mole for the SCF and CI treatments, re-

Table 2.2.5 - Basis set effect on the total energy of tetrahedral alkali-earth metal clusters^{a)}

	E_{SCF} (4 separated atoms)	$E_{\text{SCF/BE}}$	E_{CI} (4 separated atoms)	$E_{\text{CI/BE}}$
$\text{Be}_4[4s2p]$	-3.8664	-3.8848/11.5	-4.0070	-4.0336/16.7
$\text{Be}_4[4s4p/4s2p]$	-3.8664	-3.9223/35.0	-4.0170	-4.0721/34.5
$\text{Be}_4[4s2p1d]$	-3.8664	-3.8907/15.2	-4.0089	-4.0459/23.2
$\text{Mg}_4[4s2p]$	-3.1373	-3.1369/-0.2	-3.2454	-3.2459/0.3
$\text{Mg}_4[4s3p]$ ^{b)}	-3.1373	-3.1369/-0.2	-3.2449	-3.2461/0.7
$\text{Mg}_4[4s4p/4s2p]$ ^{c)}	-3.1373	-3.1369/-0.2	-3.2102	-3.2116/0.9
$\text{Mg}_4[4s2p1d]$	-3.1373	-3.1369/-0.2	-3.2483	-3.2489/0.4
$\text{Ca}_4[4s2p]$	-2.4208	-2.4199/-0.6	-2.5043	-2.5072/1.8
$\text{Ca}_4[4s3p]$ ^{b)}	-2.4208	-2.4199/-0.6	-2.5048	-2.5075/1.7
$\text{Ca}_4[4s2p1d]$	-2.4208	-2.4203/-0.3	-2.5050	-2.5089/2.5

a) All values are in au except the binding energies (BE) which are in kcal/mole. The results refer to the $[4s2p]$ optimized distance.

b) One diffuse p function was added to the $[4s2p]$ basis set.

c) The same exponents for the 3s and 3p orbitals are used.

spectively, using an optimized bond length, 4.19 a.u., very close to the value predicted on the basis of the PP calculation (4.17 a.u.).

A second set of PP calculations was performed with a $|4s4p/4s2p|$ basis set obtained adopting the same set of p functions employed by Dykstra et al. (190). The binding energies are 35.0 kcal/mole at Hartree-Fock level and 34.6 kcal/mole in CI and agree perfectly with the results of Dykstra (190) (see Table 2.2.5). Finally, the influence of d-functions was tested by adding one d-polarization function to the $|4s2p|$ basis set, which resulted in a further increase of the stability of the cluster by about 40 per cent (Table 2.2.5).

The large difference observed when the two $|4s2p|$ and $|4s4p/4s2p|$ basis sets are used demonstrates the importance of accounting for the interaction of s and p orbitals in Be_4 tetrahedron. Many authors have pointed out that the large stability of the tetrahedral arrangement is due to an effective s-p hybridization (188,191,193). This hybridization is emphasized by the data of Table 2.2.6 in which the composition of the occupied and virtual MO's are displayed. It can be seen that the a_1 and t_2 occupied valence MOs have a significant contribution of the atomic p orbitals. Be is known to form sp^3 hybrids in

Table 2.2.6 - Orbital energies and coefficients of the valence molecular orbitals of tetrahedral $\text{Be}_4^{\text{a)}$

	$1a_1$	$1t_2$	$1t_2$	$1t_2$	$2a_1$	$2t_2$	$2t_2$	$2t_2$
orbital energy (au)	-0.54781	-0.27479	-0.27479	-0.27479	-0.00667	0.04672	0.04672	0.04672
$2s$	-0.0041	0.0034	-0.0048	0.0000	-0.0001	-0.0015	0.0021	0.0000
$2s'$	-0.0267	0.0241	-0.0341	0.0000	0.0006	-0.0090	0.0127	0.0000
$2s''$	0.2493	-0.2624	0.3711	0.0000	-0.0934	0.0612	-0.0865	0.0000
$2s'''$	0.0629	-0.1031	0.1459	0.0000	0.3269	0.3098	-0.4381	0.0000
$2p_x$	-0.1453	0.1682	0.0657	0.0000	0.2884	0.2677	-0.1212	0.0000
$2p_y$	0.0000	0.0000	0.0000	0.3036	0.0000	0.0000	0.0000	-0.2573
$2p_z$	0.1028	0.1847	0.1682	0.0000	-0.2039	0.0680	0.2677	0.0000
$2p_x$	-0.0476	0.1020	0.1813	0.0000	0.3724	0.7868	-0.5365	0.0000
$2p_y$	0.0000	0.0000	0.0000	0.3256	0.0000	0.0000	0.0000	-0.5761
$2p_z$	0.0336	0.2534	0.1020	0.0000	-0.2634	0.0197	0.7868	0.0000

a) The wavefunction has been computed using the symmetry of the D_{2h} subgroup of the tetrahedron.

several well characterized complexes, e.g. $\text{Be}(\text{H}_2\text{O})_4^{2+}$, BeF_4^{2-} or polymers such as $(\text{BeF}_2)_n$, $(\text{Be}(\text{CH}_3)_2)_n$ or $(\text{BeH}_2)_n$ (218). These facts allow the hypothesis that the same hybridization effect stabilizes also small clusters or structures which contain the basic tetrahedral cage.

In order to illustrate the changes occurring in the composition of MOs with the geometry distortion the passage of two interacting Be_2 fragments from the tetrahedral arrangement to the square planar one has been studied. The Be-Be side bond length was fixed in the Be_2 units and in the final square structure to the optimum value 4.17 a.u. obtained for the Be_4 (T_d) cluster, while the separation of the two Be_2 moieties was changed to give a distorted tetrahedron of D_{2d} symmetry. The bond lengths of the structure intermediate between T_d and D_{4h} geometries have been interpolated linearly from the geometrical parameters of these two limit structures.

The binding energy of the system (Fig. 2.2.5) clearly shows that the tetrahedral structure represents a minimum with respect to the other "buckled" clusters. The transition from the T_d to the D_{4h} structure is characterized by the appearance of an energy barrier generated by the avoided crossing of the two $(a_1)^2(e_u)^4(b_2)^2$ (D_{2d}) and $(a_{1g})^2(e_u)^4(b_{2g})^2$ (D_{4h}) electronic

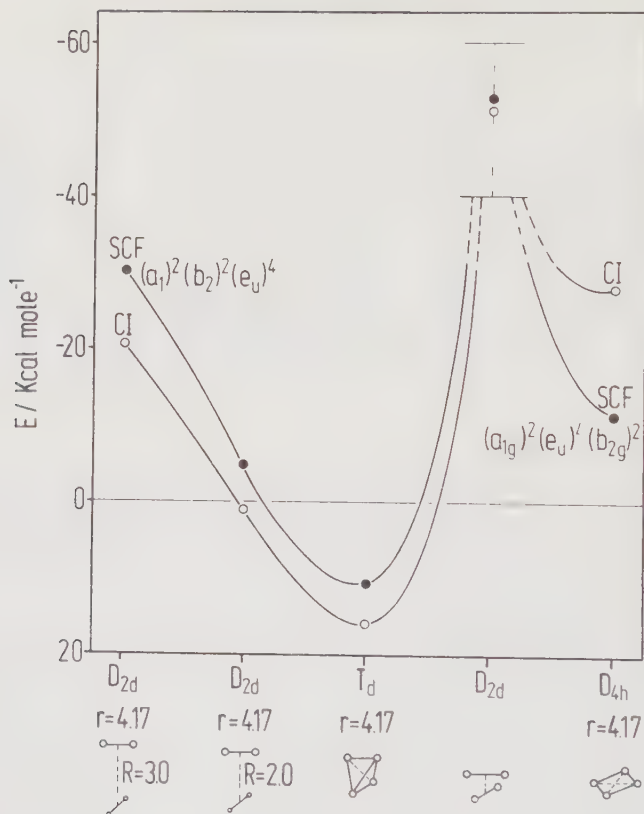


Fig. 2.2.5 - Potential energy curves at SCF and CI level for the approaching of two Be_2 moieties to yield the tetrahedral structure and for the further deformation giving finally the square geometry. The height of the energy barrier largely depends on the geometry of the intermediate structure.

configurations (Fig. 2.2.5). The height of the energy barrier depends on the detailed geometry of the intermediate D_{2d} structure and the square structure represents a non-bonding local

minimum in the reaction path.

In the two near-tetrahedral elongated structures, all the occupied MOs are mainly composed of 2s orbitals (see Fig. 2.2.6). However, moving towards the regular tetrahedron, we observe an increase of the p contribution in the occupied MOs and in particular in the bonding a_1 MO. This becomes more evident if we look at the bottom of Fig. 2.2.6 where the weights of the p_z atomic orbitals in the totally symmetric a_1 MO are shown. The shape of this curve is directly correlated with the energy of the a_1 MO itself and its maximum coincides with the minimum of the a_1 energy curve. Closer approach of the two Be_2 fragments drastically changes the composition of the antibonding b_2 orbital, so that this MO practically becomes a linear combination of p_z orbitals not too different from the π MO of a_{2u} symmetry of the final square structure.

In summary, the average of the weakly-bonding or non-bonding MO energies is practically constant (Fig. 2.2.6), and the whole stability of the system seems to be dependent on the nature and the energy of the a_1 valence MO, which, in turn, is sensitive to the degree of the p_z admixture.

The other two geometries considered, rhombic and square Be_4 , exhibit, in the $|4s2p|$ PP treatment, a bonding situation more similar to that of Be_2 than to that of tetrahedral Be_4 . In fact, very large interatomic distances and binding energies smaller than 1 kcal/mole have been found at CI level (see Table 2.2.4). The SCF potential energy curve corresponding to the lowest electronic configuration in Be_4 (D_{2h}), $(a_g)^2(b_{3u})^2(b_{2u})^2(a_g)^2$, is always repulsive; a second repulsive electronic configuration, $(a_g)^2(b_{3u})^2(b_{2u})^2(b_{1u})^2$, has a more pronounced minimum around the distance 4.0 a.u. and does not cross the first energy curve.

A different situation arises from the analysis of the Be_4 (D_{4h}) electronic structure. When side bond lengths larger than 4.8 a.u. are considered, the $(a_{1g})^2(e_u)^4(b_{1g})^2$ electronic configuration is the most stable one. At the distance 4.8 a.u. a crossing with the $(a_{1g})^2(e_u)^4(b_{2g})^2$ MO configuration is obser-

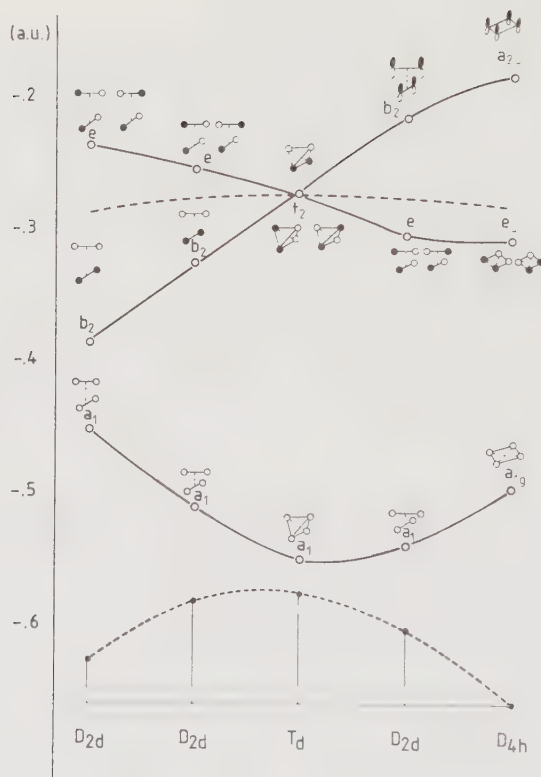


Fig. 2.2.6 - Orbital energy curves for the occupied MOs proceeding in the path from the buckled D_{2d} structure to the tetrahedral and square clusters. Along this path the a_1 MO (D_{2d} and T_d) transforms into the a_{1g} MO of the D_{4h} symmetry; the b_2 MO of the D_{2d} structure gives rise to the t_2 MOs in T_d and to the a_{2u} in D_{4h} ; finally, the degenerate e MOs of D_{2d} transform into the t_2 MOs of T_d and e_u MOs of D_{4h} . The average of the energy of the non-bonding MOs (---) is practically constant. The bottom curve (...) indicates the contribution of p_z AOs to the totally symmetric MOs. For each structure the composition of the occupied MOs in terms of atomic orbitals is shown.

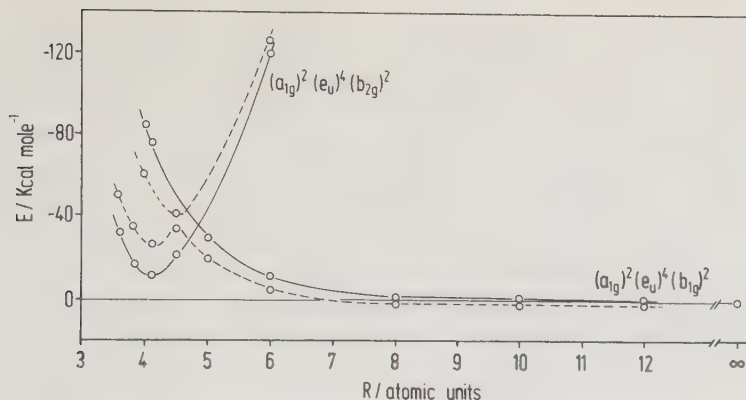


Fig. 2.2.7 - Potential energy curves for the square Be_4 (D_{4h}) cluster at PP SCF (—) and PP MRD CI (---) levels.

ved as shown in Fig. 2.2.7. Nevertheless, this latter electronic configuration corresponds to a non-bonding state at both SCF and CI levels.

While the b_{1g} orbital, of antibonding character, is mainly formed by 2s functions, the b_{2g} MO is a pure combination of in-plane 2p orbitals and is stabilized at shorter distances by the larger overlap. On the other hand, the increased overlap makes the antibonding interaction of the 2s orbitals in the b_{1g} MO stronger, rationalizing the observed crossing of the

Table 2.2.7 - Summary of the results for the $(a_{1g})^2(e_u)^4(b_{2g})$ electronic configuration of square Be_4^a

	AE STO-3G	AE 6-31G	AE [9s4p/5s2p]	AE [9s2p/5s2p]	PP [4s2p]
E_{SCF} (4 separated atoms)	-57.4071	-58.2823	-58.2891	-58.2891	-3.8664
E_{CI} (4 separated atoms)	-57.5710	-58.4051	-58.4318	-58.4242	-4.0070
Correlation energy	0.1639	0.1228	0.1427	0.1351	0.1406
$E_{\text{SCF}}(\text{Be}_4)$	-57.5053	-58.2337	-58.3128	-58.2646	-3.8491
$E_{\text{CI}}(\text{Be}_4)$	-57.6084	-58.3405	-58.4207	-58.3740	-3.9617
correlation energy	0.1032	0.1068	0.1079	0.1094	0.1126
BE SCF	61.6	-30.4	14.8	-15.4	-10.8
BE CI	23.4	-40.5	-7.0	-31.5	-28.4

a) All energies are in au except the binding energies (BE) which are in kcal/mole; in the AE calculations the CI procedure is applied only to valence electrons.

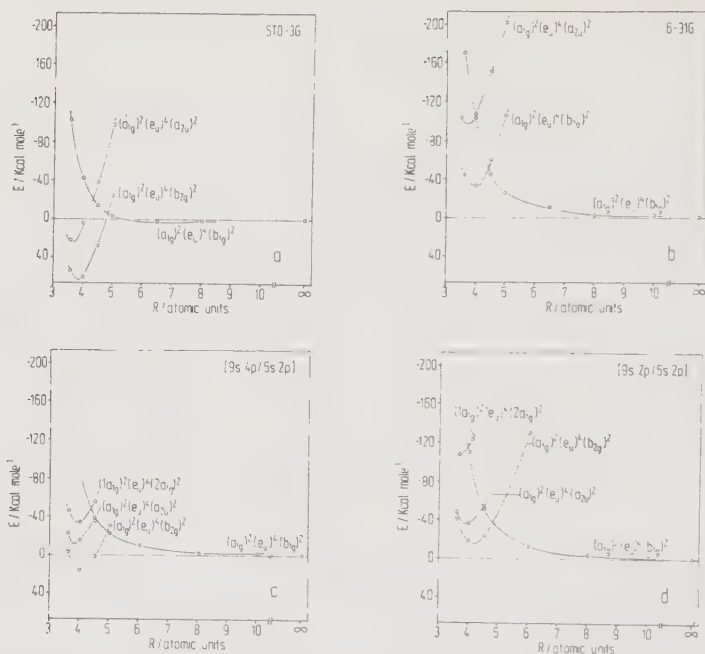


Fig. 2.2.8 - AE SCF potential energy curves for the square Be_4 (D_{4h}) cluster. (a) STO-3G basis set. (b) 6-31G basis set. (c) $|9s4p/5s2p|$ basis set. (d) $|9s2p/5s2p|$ basis set.

two potential energy curves (Fig. 2.2.7). However, in this particular case, the present PP SCF results do not agree with the AE SCF results of Whiteside et al. (197), who found a reverse ordering of the two $(a_{1g})^2(e_u)^4(b_{1g})^2$ and $(a_{1g})^2(e_u)^4(b_{2g})^2$ electronic configurations.

Since the b_{2g} MO is a pure combination of p_x and p_y atomic orbitals, a strong influence of the character of p-polarization functions on the stability of the corresponding electronic configuration is expected. We have considered this effect, computing at AE level the electronic structure of square Be_4 with four different basis sets, namely: STO-3G (219), 6-31G (220), $|9s4p/5s2p|$ (191), and the $|9s2p/5s2p|$ previously described. The relative AE Hartree-Fock curves are shown in Fig. 2.2.8.

Finally, an AE CI calculation was performed for the minimum geometry of the $(a_{1g})^2(e_u)^4(b_{2g})^2$ configuration and the corresponding results are collected in Table 2.2.7.

From the analysis of these data, it becomes evident that the use of different basis sets markedly changes the SCF results and that the inclusion of correlation effects in the MRD CI procedure moderates the influence of the AO basis set. Therefore, we can conclude that the one-electron approximation is inadequate even for qualitative predictions of this particular electronic configuration of square Be_4 (Table 2.2.7).

2.2.4.3 Be_5

Two planar and three three-dimensional Be_5 clusters have been considered: Be_5 (C_{2v}), Be_5 (D_{5h}), Be_5 (C_{4v}), Be_5 (C_s) and Be_5 (D_{3h}) (see Fig. 2.2.1 for the geometrical definitions and Table 2.2.4 for the complete results). On the basis of the previous discussion, it is not unexpected that the bipyramidal trigonal form, obtained by joining two regular tetrahedrons, shows a higher stability with respect to the other Be_5 clusters. Moreover, on going from Be_4 (T_d) to Be_5 (D_{3h}) the vertical ionization potential, computed as the difference between the neutral and the charged species, decreases from 7.68 to 6.41 eV.

The other two non-planar structures studied here are also segments of the hcp Be crystal, although in the crystal the corresponding interatomic distances are not exactly equal. The electronic structure of square pyramidal Be_5 looks very similar to that found for the square Be_4 . The best SCF electronic configuration is the $(a_1)^2(e)^4(a_1)^2(b_2)^2$ and the corresponding energy minimum (3.1 kcal/mole) is localized around the distance 4.0 a.u. .

The potential energy curves for the $(a_1)^2 \dots (b_2)^2$ electronic configuration becomes repulsive at larger distances, and at 4.8 a.u. crosses the curve of the always repulsive $(a_1)^2 \dots (b_1)^2$ molecular orbital configuration. The difference in the MO composition of these two electronic configurations reproduces the situation already described for the square case: the b_1 MO, mainly composed by in-plane s orbitals, is destabilized

at shorter distances, while the increased overlap makes the interaction of p_x and p_y orbitals in the b_2 MO stronger. The CI potential energy curve reflects this change in the MO composition and shows two different slightly bonding minima separated by an energy barrier of about 12 kcal/mole (Fig. 2.2.4d).

The Be_5 (C_s) cluster obtained by capping one triangular face of the rhombic Be_4 is the third non-planar Be_5 cluster here considered, and it represents also a section of the hcp Be crystal. The CI stability of 13.1 kcal/mole, obtained for a distance 4.15 a.u., indicates that the addition of one atom to the rhombic Be_4 in a tetrahedric coordinative position stabilizes the system much more than the planar extension of the structure to give the Be_5 (C_{2v}) cluster. This latter aggregate, in fact, is characterized by a CI potential energy curve very similar to that found for the rhombus, which is strongly repulsive at short distances and slightly attractive at larger distances.

On the contrary, the pentagonal Be_5 (D_{5h}) was found to be the most stable Be_5 cluster at Hartree-Fock level with a binding energy of 26.9 kcal/mole. This result agrees with that of Whiteside et al. (197), although the inclusion of the MRD CI procedure reduces this value to about 12 kcal/mole. The appreciable stability and the short equilibrium distance (4.2 a.u.) of this cluster with respect to the other planar structures is not surprising and can be rationalized on the basis of the smaller geometrical strain of the pentagonal arrangement, where the Be-Be-Be angles of 128° are not too far from the classical angle of the sp^2 hybrid. The effect of the short-range p-interaction is well evidenced by the CI potential energy curves of Be_5 (D_{3h}), Be_5 (D_{5h}) and Be_5 (C_{4v}) reported in Fig. 2.2.4 b, c and d, respectively, where the important changes in the electronic structures related to the distance modifications are responsible for the two minima observed.

2.2.4.4 Be_6 -

For the study of these larger Be clusters we have adopted the $|4s4p/4s2p|$ basis set in order to assure a good description

of the s-p interaction. Four different structures have been considered as shown in Fig. 2.2.1. Three of these structures, Be_6 (D_{2h}), Be_6 (O_h) and Be_6 (C_{2v}') are regular fragments of the hcp lattice, while the Be_6 (C_{2v}) is obtained by twisting the Be_6 (D_{2h}) cluster up to obtain three condensed tetrahedrons.

All these clusters are characterized by a short equilibrium distance and by a considerable stability also in the SCF treatment (Table 2.2.4). The Be_6 (D_{2h}) cluster, obtained by growing in a symmetrical way the Be_5 (C_s) one, is the most stable Be_6 cluster, with a CI binding energy of 54.5 kcal/mole. Despite the fact that the basis sets used for the two Be_5 (C_s) and Be_6 (D_{2h}) clusters are not comparable, it is evident that the large stability of the Be_6 (D_{2h}) structure is due to the possibility for the edge-atom of the pentamer to form strong bonds when the added atom is in a tetrahedrally coordinative position.

The same observation holds for the octahedron Be_6 , where the sixth atom added to the square pyramidal Be_5 plays a fundamental role in the stabilization of the cluster making possible a perfectly uniform participation of all p AOs to the bond.

In the more compact C_{2v} cluster, the higher electronic energy is compensated by the stronger nuclear repulsion and the final result is that this cluster is 3 kcal/mole less stable than the corresponding Be_6 (D_{2h}) cluster. The second Be_6 cluster of C_{2v} symmetry can be considered as an intermediate step of the growth of the planar cluster from rhombic to the symmetrical Be_7 (D_{6h}) discussed in Section 2.2.5.1. The relative binding energy of 36.3 kcal/mole in CI indicates that the stability of planar structures increases with the number of nearest neighbors. The electronic ground state configuration $(a_1)^2(b_2)^2(a_1')^2(b_2')^2(a_1'')^2(b_1'')^2$, is characterized by the presence of the highest occupied MO of b_1 symmetry, which is an in-phase combination of p_z orbitals.

However, this planar cluster is the less stable among Be_6 clusters here considered, and the final ordering of the stabilities of the four geometries, $D_{2h} > C_{2v} > O_h > C_{2v}'$, supports once more the conclusion that tetrahedral arrangements are preferred, at least when small clusters are considered.

The two clusters Be_6 (D_{2h}) and Be_6 (C_{2v}') have their triplet states 10 and 5 kcal/mole above the corresponding singlets (see Table 2.2.4) for the interatomic distance 3.8 a.u. (D_{2h}) and 4.0 a.u. (C_{2v}').

2.2.4.5 Basis set for larger Be clusters

For the planar structure of seven Be atoms here investigated a $|4s4p/3s2p|$ basis set was adopted in which the two inner s Gaussian functions have been contracted (Table 2.2.1). The geometry of this cluster, which represents a section of the hcp Be crystal lattice, is characterized by the presence of six peripheral atoms interacting with a single central atom. The situation is very different from that of the other planar structures considered, because here there are no corner atoms to form strained angles with the two nearest neighbors and reflect the situation of atoms in a Be monolayer.

For this geometrical arrangement the triplet SCF energy is much lower than the singlet one, but when correlation effects are considered the two electronic states are energetically very close.

The presence of the central atom is crucial for the stabilization of the structure and seems to produce an effect similar to that shown by the apical atoms in Be_6 (D_{2h}) or Be_6 (O_h).

We have calculated the same Be_7 cluster with the nearly minimal basis set $|4s4p/2s1p|$ described in the computational section in order to test the possible extension of the investigation to larger Be clusters. The ordering and the composition of the occupied MOs are very similar for both basis sets used. Also for this minimal basis set the triplet energy is much lower than the singlet one in SCF while the singlet-triplet splitting nearly disappears in the CI procedure. This small basis set is capable of providing a good qualitative description of Be clusters containing a larger number of atoms, and therefore has been adopted for the investigation of medium-size Be clusters.

2.2.5 Medium-size Be_n clusters ($n = 7, 10, 13$)

The Be clusters investigated (Fig. 2.2.2) are deformed sections (either planar or non-planar) of the hcp Be crystal lattice with all Be-Be distances identical. While for the $\text{Be}_7(7,0)$ cluster a complete analysis of the potential energy curves has been carried out, for the larger Be_n clusters ($n = 10, 13$) the Be-Be bond length has been fixed to the experimental value 4.2 a.u. for the nearest neighbor interatomic distance in the hcp Be crystal (221). This is a reasonable assumption because the optimized bond distances for the smaller Be aggregates fall always in a small range around this value. Moreover, the interatomic distances for the equilibrium geometry of the $\text{Be}_7(7,0)$ cluster are very close to the Be-Be distance in the crystal. The average distance 4.2 a.u. between neighboring atoms in a cluster seems to be independent from the cluster geometry and can be rationalized by the same kind of chemical bonding present in clusters and the bulk metal.

In addition to the previously carefully tested Be_4 system, the reliability of the PP MRD CI approach for the investigation of medium-size Be clusters has been specifically tested for the $\text{Be}_7(7,0)$ cluster. For this structure a complete analysis of the low-lying singlet and triplet states has been carried out by means of both PP MRD CI and AE MRD CI treatments. The AE basis set used $|9s4p/5s1p|$ has been taken from Yarkony and Schaefer (205). The agreement between the two sets of results is very satisfactory as will be shown later. In particular, the ordering of the different states and the computed dissociation energies are well reproduced in the PP framework. Small differences have been found in the equilibrium bond distances which in PP are slightly larger than in AE. This may be attributed to the core-polarization effects being neglected in the PP procedure employed.

Three points of particular interest are analyzed in this paragraph: a) the influence of correlation effects on the ordering of the electronic states of Be clusters; b) the existence of many close-lying states of singlet or triplet multiplicity

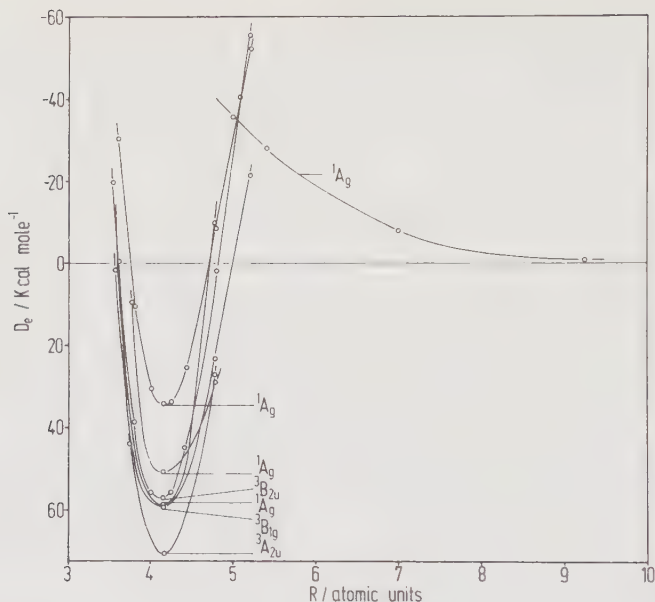


Fig. 2.2.9 - PP SCF potential energy curves for the low-lying electronic configurations of $\text{Be}_7(7,0)$ cluster. See scheme I and Table 2.2.9 for definitions.

in the clusters; c) the possible reasons for the comparable stability of planar and non-planar medium-size cluster.

2.2.5.1 Be_7

The PP energy curves for planar Be_7 are reported in Fig. 2.2.9 (SCF) and 2.2.10 (CI). The PP CI energy curves of Fig. 2.2.10 exhibit a characteristic double minimum due to the appearance of two different kind of bonding in these aggregates. The first deep minimum, at a Be-Be nuclear separation very close to that of the crystal, is due to the large s-p hybridization which is responsible for the considerable stability of these clusters. As shown in Fig. 2.2.9 and 2.2.10 the position of this inner minimum is nearly the same for both singlet and triplet states.

On the other hand, the interaction of n Be atoms in their

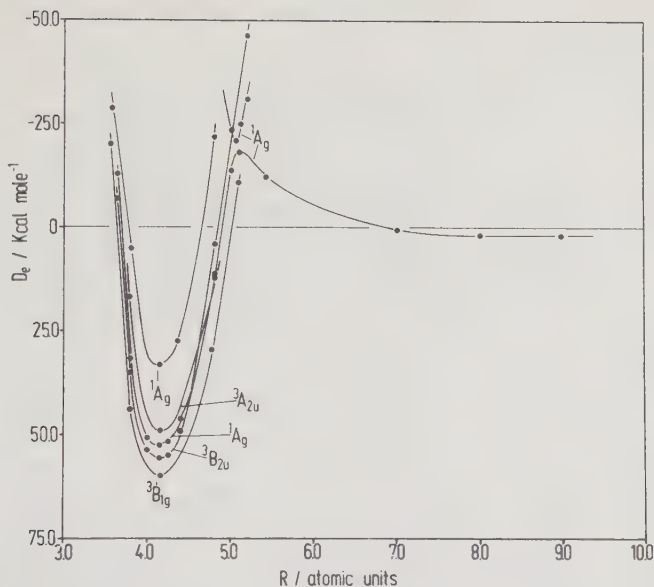
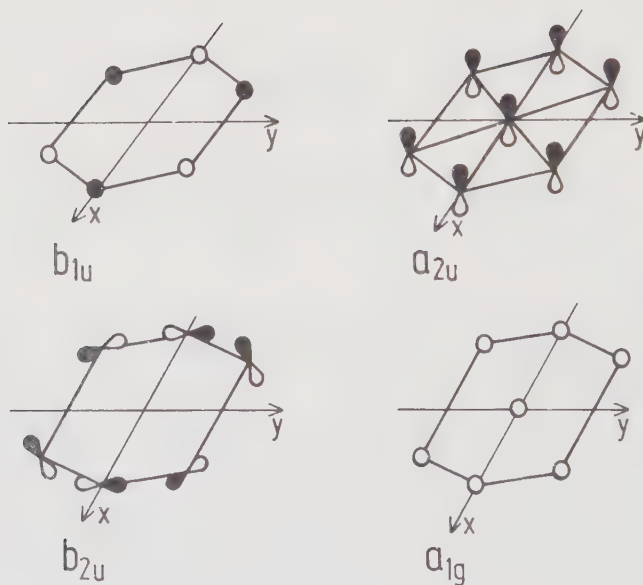


Fig. 2.2.10 - PP MRD CI potential energy curves for the low-lying states of $\text{Be}_7(7,0)$ cluster. See scheme I and Table 2.2.9 for definitions.

$1s(2s^2)$ ground state configuration gives rise to a weak attractive interaction at a distance of about 9 a.u. in the CI treatment. The different nature of the binding at the two minima is well documented by the results of population analysis (Table 2.2.8). While the electronic configuration of the Be atoms at the larger distance is very close to that of the free atom, a strong electronic redistribution occurs as the internuclear separation approaches the value 4.2 a.u. The stabilization gained with the formation of the bonds compensates the energy necessary to promote electrons from the 2s to the 2p orbitals so that the final electronic distributions on Be atoms correspond to sp hybrids. A maximum due to the avoided crossing of two $1A_g$ states separates the two minima. The energies of two electronic configura-

Table 2.2.8 - Average population analysis of Be clusters

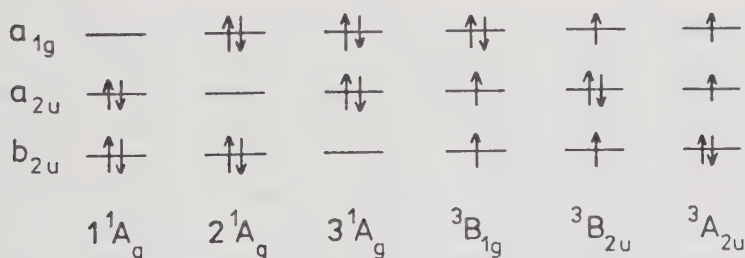
	$\text{Be}_7(7,0) {}^1\text{B}_{1g}$ $R = 4.15 \text{ au}$	$\text{Be}_7(7,0) {}^1\text{A}_{1g}$ $R = 9.0 \text{ au}$	$\text{Be}_{10}(10,0) {}^1\text{A}_g$ $R = 4.2 \text{ au}$
2s	0.845	1.920	0.670
2p _{x,y}	1.004	0.055	1.125
2p _z	0.151	0.024	0.204
	$\text{Be}_{10}(7,3) {}^1\text{A}_1$ $R = 4.2 \text{ au}$	$\text{Be}_{13}(13,0) {}^1\text{A}_g$ $R = 4.2 \text{ au}$	$\text{Be}_{11}(3,7,3) {}^1\text{E}''$ $R = 4.2 \text{ au}$
2s	0.722	0.673	0.631
2p _{x,y}	0.867	1.170	0.905
2p _z	0.411	0.157	0.463

Fig. 2.2.11 - Symmetries and shapes of highest occupied MOs of $\text{Be}_7(7,0)$ (see scheme I).

tions $(1a_{1g})^2(e_{1u})^4(e_{2g})^4(2a_{1g})^2(b_{1u})^2$ and $(1a_{1g})^2(\dots)(2a_{1g})^2(a_{2u})^2$ cross at the distance 5.0 a.u. in the SCF approximation. The composition of the b_{1u} and a_{2u} MOs (Fig. 2.2.11) clearly indicates the different participation of p atomic orbitals in these two configurations.

The electronic structure of $\text{Be}_7(7,0)$ in the region of energy minimum is characterized by a set of energetically low-lying fully occupied MOs $(a_{1g})^2(e_{1u})^4(e_{2g})^4$ followed by three very close spaced MOs, namely b_{2u} , a_{2u} and a_{1g} (Fig. 2.2.11). Six possible electronic configurations are generated by the distribution of the remaining four valence electrons in these MOs:

Scheme I



The SCF and CI energies and equilibrium bond distances for these six molecular states obtained with AE and PP methods are reported in Table 2.2.9. As already noted in the computational section, no significant differences have been found between the AE and PP approaches, so that the following discussion holds for both sets of results.

At SCF level the ground state of Be_7 is the $3A_{2u}$ corresponding to the electronic configuration $(1a_{1g})^2(\dots)(b_{2u})^2(a_{2u})^1(2a_{1g})^1$. The first singlet state, 1^1A_g , with the configuration $(1a_{1g})^2(\dots)(b_{2u})^2(a_{2u})^2$ is separated by 13 kcal/mole from the $3A_{2u}$ ground state. However, this energy ordering is completely changed when correlation effects are taken into account. The ground state is a triplet of B_{1g} symmetry with the leading configuration $(1a_{1g})^2(\dots)(2a_{1g})^2(b_{2u})^1(a_{2u})^1$ followed by a second

Table 2.2.9 - Comparison of PP and AE results for the $\text{Be}_7(7,0)$ cluster^{a)}

		1^1A_{1g}	2^1A_{1g}	3^1A_{1g}	$3B_{1g}$	$3B_{2u}$	$3A_{2u}$
E_{NCF}	(PP)	-6.8602	-6.8543	-6.8210	-6.8611	-6.8585	-6.8805
	(AE)	-102.1036	-102.0924	-102.0585	-102.0986	-102.0983	-102.1194
E_{CI}	(PP)	-7.0247	-7.0334	-7.0542	-7.0651	-7.0579	-7.0477
	(AE)	-102.2704	-102.2700	-102.2946	-102.3055	-102.3004	-102.2888
E_{corr}	(PP)	0.1645	0.1791	0.2332	0.2040	0.1994	0.1672
	(AE)	0.1668	0.1776	0.2361	0.2069	0.2021	0.1694
$r_e(\text{SCF})$	(PP)	4.08	4.31	4.19	4.24	4.13	4.21
	(AE)	4.01	4.29	4.15	4.21	4.07	4.16
$r_e(\text{CI})$	(PP)	4.09	4.32	4.18	4.23	4.15	4.24
	(AE)	4.02	4.31	4.12	4.22	4.08	4.19
$D_e(\text{SCF})$	(PP)	59.0	55.2	34.4	59.5	57.8	71.7
	(AE)	61.2	54.2	33.0	58.1	57.9	71.2
$D_e(\text{CI})$	(PP)	35.8	41.3	54.3	61.2	56.7	50.3
	(AE)	42.0	41.7	57.2	64.0	60.8	53.5

^{a)} Energies and equilibrium bond distances (r_e) in au, dissociation energies (D_e) in kcal/mole.

triplet, $3B_{2u}$. The first $1A_g$ state lies about 6 kcal/mole above the ground state (Figs. 2.2.9 and 2.2.10 and Table 2.2.9).

The reverse ordering in CI can be explained on the basis of the different lowering of the total energy due to the electron correlation corrections (Table 2.2.9). In particular, the estimated correlation energy is minimal when the b_{2u} MO is fully occupied ($E_{\text{corr}} = 0.16\text{--}0.18$ a.u.), reaches its maximum when the b_{2u} MO is empty ($E_{\text{corr}} = 0.23$ a.u.) and is intermediate when the b_{2u} MO is singly occupied ($E_{\text{corr}} = 0.20$ a.u.) (see Scheme I and Table 2.2.9).

To this point the analysis of the electronic structure of Be_7 presents some analogies with the case of square Be_4 , where the occupation of the b_{2g} valence MO which is a linear combination of in-plane p-orbitals, stabilizes the corresponding electronic configuration in SCF much more than in CI.

The obtained AE CI binding energy for the $3B_{1g}$ ground state, 60 kcal/mole, is much larger than that computed by Bauschlicher et al. (200,201) at SCF level for the same Be_7 cluster. These authors have found for the closed shell electronic configuration $(1a_{1g})^2(\dots)(2a_{1g})^2(b_{2u})^2$ a dissociation energy of 25.5 kcal/mole (200,201) which corresponds to 50 per cent of our SCF computed values for the same configuration (Table 2.2.9). Adopting

the more flexible $|4s4p/3s2p|$ PP basis set we have computed for the Be_7 cluster a dissociation energy of about 80 kcal/mole in both SCF and CI treatments.

The total AE SCF energy for the 2^1A_{1g} configuration reported in ref. (188) is -100.783 a.u. while our AE basis set yields for the same configuration the energy -102.092 (Table 2.2.9). The higher energy found by Bauschlicher et al. may be attributed to the use of a set of less flexible p-polarization functions than was used in our case.

2.2.5.2 Be_{10} -

$\text{Be}_{10}(10,0)$ is a planar extension of the $\text{Be}_7(7,0)$ cluster, while $\text{Be}_{10}(7,3)$ serves to represent three dimensional clusters. The $\text{Be}_{10}(7,3)$ cluster, of C_{2v} symmetry, contains three tetrahedral units with one common vertex.

In Table 2.2.10 and 2.2.11 are given the PP results for these two clusters. Six SCF electronic states have been investigated in the case of planar Be_{10} . These corresponds to different

Table 2.2.10 - Results for the $\text{Be}_{10}(10,0)$ cluster^{a)}

	1^1A_g	2^1A_g	3^1A_g	3^1B_{3u}	3^1B_{2g}	3^1A_u
E_{SCF}	-9.8905	-9.7635	-9.7686	-9.8441	-9.8384	-9.7841
E_{CI}	-10.1212	-10.0340	-10.0292	-10.0948	-10.0862	-10.0661
E_{corr}	0.2307	0.2705	0.2606	0.2507	0.2478	0.2820
$D_e(\text{SCF})$	140.8	61.1	64.3	111.7	108.1	74.1
$D_e(\text{CI})$	117.9	63.2	60.2	101.4	96.0	83.4

^{a)} The results refer to the non-optimized Be-Be bond distance 4.2 au. Energies in au, dissociation energies (D_e) in kcal/mole.

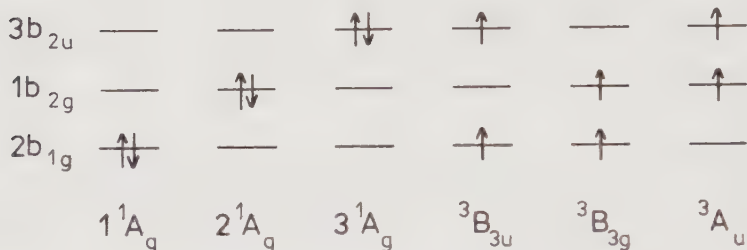
Table 2.2.11 - Results for the $\text{Be}_{10}(7,3)$ cluster^{a)}

	1^1A_1	2^1A_1	3^1A_1	1^1E	2^1E
E_{SCF}	-9.8372	-9.7953	-9.8366	-9.8304	-9.8367
E_{CI}	-10.1219	-10.0709	-10.1025	-10.1045	-10.1043
E_{corr}	0.2847	0.2756	0.2659	0.2741	0.2676
$D_e(\text{SCF})$	107.4	81.1	107.0	103.1	107.1
$D_e(\text{CI})$	118.4	86.4	106.2	107.5	107.4

^{a)} The results refer to the non-optimized Be-Be bond distance 4.2 au. Energies in au, dissociation energies (D_e) in kcal/mole.

electronic configurations arising from the possible occupations of the three highest $2b_{1g}$, $1b_{2g}$ and $3b_{2u}$ valence MOs:

Scheme II



Consequently, the six valence electronic configurations can be in closed form written as $(1a_g)^2(1b_{3u})^2(1b_{2u})^2(2a_g)^2(1b_{1g})^2(2b_{3u})^2(2b_{2u})^2(3a_g)^2(1b_{1u})^2(2b_{1g})^x(1b_{2g})^y(3b_{2u})^z$ with $x, y, z = 0, 1, 2$. The shapes of the six highest MOs of $\text{Be}_{10}(10,0)$ are shown in Fig. 2.2.12. The $(1a_g)^2(\dots)(2b_{1g})^2$ valence electronic configuration is the most stable one followed by two open shell configurations, $(1a_g)^2(\dots)(2b_{1g})^1(3b_{2u})^1$ and $(1a_g)^2(\dots)(2b_{1g})^1(1b_{2g})^1$.

The correlation effects reduce the SCF dissociation energy but the sequence of the three lowest states 1^1A_g , 3^3B_{3u} and 3^3B_{3g} parallels the ordering of the electronic configurations found at SCF level (Table 2.2.10). Therefore, the ground state of the cluster is a singlet separated by about 16 kcal/mole from the lowest triplet.

Four nearly degenerated molecular states characterize the electronic structure of the more compact $\text{Be}_{10}(7,3)$. Three of these states are triplets (Table 2.2.10). The lowest closed shell electronic configuration is found to be the $(1a_1)^2(1e)^4(2a_1)^2(2e)^4(3a_1)^2(4a_1)^2(3e)^4$ with a SCF $D_e = 107.4$ kcal/mole. The CI treatment lowers the total energy of the 1^1A_g state more than that of the triplet states so that the final CI ground state is a singlet ($D_e = 118$ kcal/mole) with the three lowest triplet

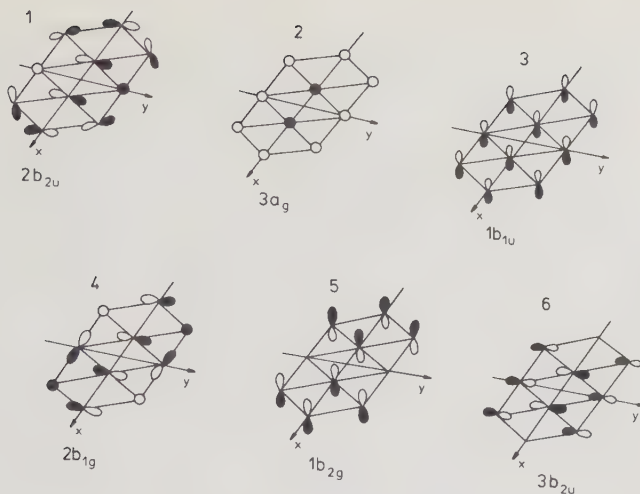


Fig. 2.2.12 - Symmetries and shapes of highest occupied MOs of $\text{Be}_{10}(10,0)$ in the sequence according the increasing MO-energy (see scheme II).

states lying only 10 kcal/mole above the ground state.

The computed CI dissociation energy for the $\text{Be}_{10}(7,3)$ cluster, 118.4 kcal/mole, is virtually identical to the corresponding one of the planar Be_{10} (117.9 kcal/mole). Therefore, both these structures have a binding energy per atom larger than that computed for the Be_7 cluster. In comparison with the latter aggregate, we have found that in Be_{10} clusters the s-p hybridization (as measured by the population analysis) is about 20 per cent larger (Table 2.2.8). These results are in qualitative agreement with those of Bauschlicher et al. (200), even if these authors obtained an increase of the binding energy per atom going from Be_7 to Be_{10} (5.3 kcal/mole) which is markedly larger than our computed value (3.3 kcal/mole). However, this discrepancy must be attributed to the small stability found by these authors for the $\text{Be}_7(7,0)$ cluster (200).

The large stability of planar Be_{10} can be understood by a more detailed analysis of the electronic structure of the clu-

ster. The analogies between the shapes of the highest occupied MOs of Be_7 (Fig. 2.2.11) and $\text{Be}_{10}(10,0)$ (Fig. 2.2.12) are evident. With the exception of the $2a_{1g}$ and $3a_g$ MOs of Be_7 and Be_{10} , respectively, which are essentially formed by 2s atomic orbitals, all other MOs are mainly composed from 2p atomic orbitals. In particular, some MOs of Be_{10} are linear combinations of in-plane p-orbitals with different bonding character. As for Be_7 , also in $\text{Be}_{10}(10,0)$ the bonding combination of p_z orbitals generates a MO of b_{1u} symmetry which plays a very important role in the stabilization of the cluster.

Those electronic configurations where the $1b_{1u}$ MO of $\text{Be}_{10}(10,0)$ is empty or half-occupied are unfavourable with respect to configurations which contain the b_{1u} MO doubly-occupied. The b_{1u} is not the only important linear combination of $2p_z$ atomic orbitals of Be_{10} . The $1b_{2g}$ MO (Fig. 2.2.12) is in fact a combination of p_z orbitals with lower bonding character. Because of its slightly antibonding nature, the electronic configurations in which the $1b_{2g}$ orbital is partially or totally filled are not very energetically favourable (see Scheme II and Table 2.2.10).

Therefore, the stability of the $\text{Be}_{10}(10,0)$ cluster has to be attributed both to the strong overlap of the sp hybrid orbitals in the plane of the Be atoms and to the formation of a MO having similar characteristics as those of delocalized π MOs in graphite or in unsaturated hydrocarbons.

On the contrary, in the non-planar $\text{Be}_{10}(7,3)$ cluster the p_z orbitals are strongly involved in the bonding between layers, and the whole structure is stabilized by sp-type hybrids.

The different role of p_z atomic orbitals in the two structures $\text{Be}_{10}(10,0)$ and $\text{Be}_{10}(7,3)$ is well emphasized by the data of Mulliken population analysis (Table 2.2.8). In $\text{Be}_{10}(10,0)$, where the p_z atomic orbitals contribute to a singly occupied MO, the average $2p_z$ atomic population (CI) is 0.2, while this value is about twice in $\text{Be}_{10}(7,3)$ because of the strong participation of p_z orbitals to the bonding between different layers of beryllium atoms.

2.2.5.3 Be₁₃-

Tables 2.2.12 and 2.2.13 show the results for the two largest Be clusters considered: the planar Be₁₃(13,0) and the non-planar Be₁₃(3,7,3) (Fig. 2.2.2).

Be₁₃(13,0) is characterized at SCF level by a triplet ground state corresponding to the valence electronic configuration $(1a_g)^2(1b_{3u})^2(2a_g)^2(1b_{2u})^2(1b_{1g})^2(2b_{3u})^2(3a_g)^2(2b_{1g})^2(3b_{2u})^2(4a_g)^2(3b_{3u})^2(1b_{1u})^1(1b_{2g})^1$. The composition of the six highest occupied MOs of Be₁₃(13,0) is shown in Fig. 2.2.13.

As in the case of Be₁₀(10,0), the SCF dissociation energy of Be₁₃(13,0) is larger than the CI value (10 per cent). Moreover, the inclusion of electron correlation changes the ordering of the molecular states and yields the ground state 1A_g with the leading configuration $(1a_g)^2 \dots (3b_{3u})^2(1b_{1u})^2$ yielding the stability of 201 kcal/mole for dissociation into Be atoms. The singlet-triplet splitting, corresponding to the excitation of one electron from the bonding $1b_{1u}$ MO to the partially anti-bonding $1b_{2g}$ MO (Fig. 2.2.12) is only 7.6 kcal/mole and therefore-

Table 2.2.12 - Results for the Be₁₃(13,0) cluster^{a)}

	1A_g	2A_g	3A_g	$^3B_{1u}$	$^3B_{2g}$	$^3B_{2u}$
E_{SCF}	-12.9055	-12.8274	-12.7919	-12.9227	-12.8830	-12.8359
E_{CI}	-13.1935	-13.1217	-13.1181	-13.1815	-13.1569	-
E_{corr}	0.2879	0.2943	0.3262	0.2588	0.2737	-
$D_e(SCF)$	213.1	164.1	141.8	223.9	199.0	169.5
$D_e(CI)$	201.5	156.1	154.2	193.9	178.5	-

^{a)} The results refer to the non-optimized Be-Be bond distance 4.2 au. Energies in au, dissociation energies (D_e) in kcal/mole.

Table 2.2.13 - Results for the Be₁₃(3,7,3) cluster^{a)}

	$^1A'_1$	$^2A'_1$	$^3E''$	$^3E'$
E_{SCF}	-12.8471	-12.8747	-12.8821	-12.8371
E_{CI}	-13.1938	-13.2180	-13.2263	-13.2124
E_{corr}	0.3466	0.3432	0.3442	0.3393
$D_e(SCF)$	176.5	193.8	198.4	192.8
$D_e(CI)$	201.7	216.9	222.1	213.4

^{a)} The results refer to the non-optimized Be-Be bond distance 4.2 au. Energies in au, dissociation energy (D_e) in kcal/mole.

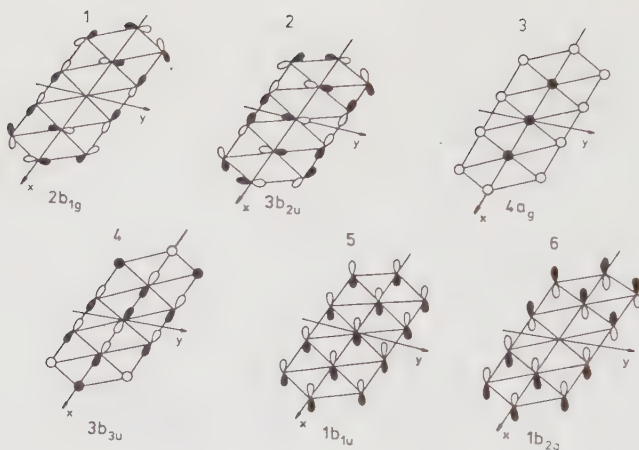


Fig. 2.2.13 - Symmetries and shapes of highest occupied MOs of $\text{Be}_{13}(13,0)$ in the sequence according to the increasing MO energy.

re the two states can be considered as virtually degenerated.

The similarities between the MOs of $\text{Be}_{13}(13,0)$ and those of $\text{Be}_{10}(10,0)$ (Fig. 2.2.12 and 2.2.13, respectively) are evident. For the largest planar cluster here considered the π -type $1b_{1u}$ MO (analogous to a_{2u} for $\text{Be}_7(7,0)$) is doubly-occupied in the ground state, and the relatively large dissociation energy of this structure must be partially attributed to this MO and to the planar bonding originated by p_x and p_y atomic orbitals in the other MOs as well. This kind of interaction gets more and more important as the cluster size increases so that whereas very small planar Be clusters like rhombus Be_4 are rather unstable, the $\text{Be}_{13}(13,0)$ cluster displays a comparable stability to that of the more compact $\text{Be}_{13}(3,7,3)$ (Table 2.2.12 and 2.2.13).

For the $\text{Be}_{13}(3,7,3)$ cluster we have found at least four states having very similar energies (Table 2.2.13). The 3E is the ground state of the system in both SCF and CI. However, the CI space to which the total energy of the system is extrapolated

ted is very large compared to the number of selected configurations (Table 2.2.2). Therefore, this prediction of the molecular ground state is unreliable because the error introduced by the extrapolation procedure can exceed the small energy differences existing between states of different spin multiplicity.

It is worth noting that some features found for Be_{10} clusters are confirmed by the results for the larger Be_{13} systems. In particular, the presence of many nearly degenerated singlet and triplet states is more pronounced in the case of more compact structures, such as $\text{Be}_{10}(7,3)$ and $\text{Be}_{13}(3,7,3)$ (Tables 2.2.12 and 2.2.13).

Bauschlicher, Bagus and Schaefer III (201) explain the existence of energetically low-lying triplet states in large Be clusters as due to the edge effects. For the $\text{Be}_{13}(10,3)$ cluster they found that the electron density of the singly occupied MOs is localized on few atoms on the border of the cluster. However, electron density analysis performed for our $\text{Be}_{13}(13,0)$ and $\text{Be}_{13}(3,7,3)$ clusters shows that the electron density of the open shell MOs is delocalized over many atomic centers and that these centers are not necessarily localized on the edges of the cluster. The localization of the frontier orbitals of $\text{Be}_{13}(10,3)$ is probably due to the three atoms on the second layer which induce an asymmetrical situation for some atoms belonging to the top layer of the cluster. This conjecture is supported also by the results obtained for Be_{10} clusters and in particular for $\text{Be}_7(7,0)$ where the open shell electron density is mainly concentrated on the central Be atom.

The different nature of the bonding in the planar and non-planar Be_{13} clusters is clear from the CI population analysis (Table 2.2.8). In comparison with the results obtained for $\text{Be}_{10}(10,0)$ and $\text{Be}_{10}(7,3)$ clusters, in $\text{Be}_{13}(13,0)$ we note a slightly increased involvement of the in-plane p-orbitals in the bond with respect to the p_z orbitals. Moreover, the presence of the third layer in $\text{Be}_{13}(3,7,3)$ produces a flow of electrons from the 2s to the $2p_{x,y}$ and quite naturally even more to the $2p_z$ atomic orbitals of Be (Table 2.2.8).

The enlargement of the cluster is accompanied by a pronounced electronic redistribution between 2s and 2p AOs. An appreciable increase of the relative stability of the cluster measured by the binding energy per atom is observed (the respective values of the binding energy per atom for the most stable Be_7 , Be_{10} and Be_{13} clusters are 8.6, 11.8 and 17.0 kcal/mole).

2.2.6 Mg_n clusters ($n = 3, 4, 5$)

Few experimental work has been done on Mg clusters. Recently the MCD spectra of matrix isolated Mg_3 and Mg_4 has been reported (222). The existence of small Mg aggregates has been demonstrated (223) and other experimental data are becoming available (224,225) for crystallites having sizes in the range from few tens to some hundreds of atoms. As of yet, these structures are outside the range of present computation capabilities.

Mg_n clusters have been investigated in the framework of the PP MRD CI method using the $|4s2p|$ basis set described in the computational part (Table 2.2.1). Tetrahedral Mg_4 has been studied in greater detail adopting a larger basis set in order to demonstrate the importance of d-functions for these clusters.

2.2.6.1 Mg_3

As for the Be_3 clusters, neither linear nor triangular Mg_3 show an appreciable stability (Table 2.2.14) and also the small

Table 2.2.14 - Electronic properties of Mg clusters ^{a)}

	Side bond length	E_{SCF} singlet	E_{SCF} triplet	$E_{\text{CI/BE}}$ singlet	$E_{\text{full CI/BE}}$ singlet	IP
$\text{Mg}_3(\text{D}_{3h})$	11.2	-2.3528	-2.2693	-2.4383/0.14	-2.4514/0.21	7.16
$\text{Mg}_3(\text{D}_{\infty h})$	11.3	-2.3529	-2.2698	-2.4382/0.11	-2.4513/0.14	7.13
$\text{Mg}_4(\text{T}_d)$	11.0	-3.1369	-2.9877	-3.2459/0.33	-3.2655/0.43	7.10
$\text{Mg}_4(\text{D}_{4h})$	11.2	-3.1371	-2.9277	-3.2458/0.26	-3.2653/0.31	7.03
$\text{Mg}_4(\text{D}_{2h})$	11.2	-3.1369	-3.0535	-3.2458/0.26	-3.2654/0.36	7.10
$\text{Mg}_4(\text{C}_{2v})$	9.8	-3.1370	-3.0547	-3.2457/0.20	-3.2652/0.26	7.04
$\text{Mg}_4(\text{D}_{\infty h})$	11.4	-3.1374	-3.0533	-3.2456/0.17	-3.2651/0.20	7.08
$\text{Mg}_5(\text{D}_{3h})$	10.9	-3.9210	-3.8381	-4.0519/0.46	-4.0781/0.62	7.00
$\text{Mg}_5(\text{C}_{4v})$	11.2	-3.9212	-3.8378	-4.0518/0.40	-4.0780/0.53	6.99
$\text{Mg}_5(\text{C}_{2v})$	11.2	-3.9212	-3.8381	-4.0513/0.09	-4.0772/0.04	7.01
$\text{Mg}_5(\text{D}_{5h})$	11.3	-3.9214	-3.8377	-4.0512/0.03	-4.0772/0.04	7.05

a) All values are in au except the binding energies (BE) and the ionization potentials (IP) which are in kcal/mole and in eV respectively.

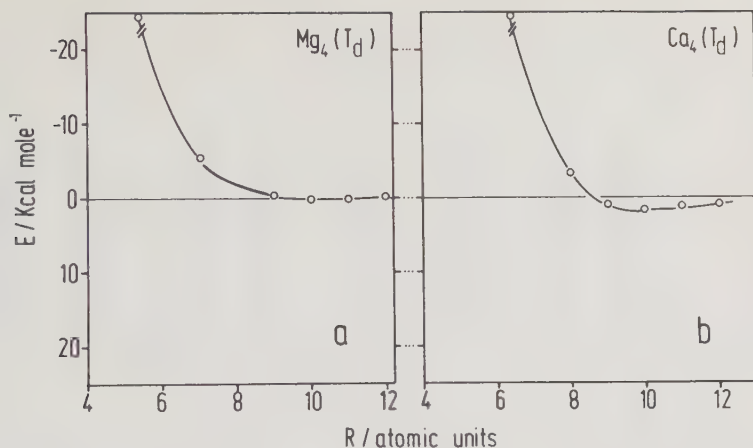


Fig. 2.2.14 - Potential energy curves for the ground state of tetrahedral Mg_4 (a) and Ca_4 (b) clusters. The curves have been obtained using a basis set which does not include d-polarization functions.

dissociation energy found is due only to the correlation effects. The $^1\Sigma_g^+$ ground state of linear Mg_3 and the corresponding $^1A_1'$ ground state of triangular Mg_3 have their potential energy minima at a nuclear separation larger than that found in the Mg_2 molecule.

As in the case of linear Be_3 the $^3\Sigma_u^+$ state of linear Mg_3 exhibits a pronounced minimum at a much shorter distance (8.0 a.u.), but the lowest triplet energy lies about 50 kcal/mole above the limit of dissociation into three Mg atoms. This energy gap is even more pronounced when we consider the two $^1A_1'$ and $^3E'$ potential energy curves of triangular Mg_3 .

2.2.6.2 Mg_4 -

Five different structures have been considered, namely tetrahedron (T_d), square (D_{4h}), rhombus (D_{2h}), T-form (C_{2v}) and linear ($D_{\infty h}$) (Fig. 2.2.1). The optimized bond lengths and the computed dissociation energies are given in Table 2.2.14. For

Table 2.2.15 - Orbital energies and coefficients of the valence molecular orbitals of tetrahedral Mg_4 ^{a)}

	1a ₁	1t ₂	1t ₂	1t ₂	2a ₁	2t ₂	2t ₂	2t ₂
orbital energy (au)	-0.26442	-0.24794	-0.24794	-0.24794	0.07409	0.09417	0.09417	0.09417
3s	-0.0066	0.0070	-0.0098	0.0000	-0.0018	-0.0007	0.0010	0.0000
3s'	-0.0645	0.0682	-0.0964	0.0000	-0.0365	-0.0201	0.0284	0.0000
3s''	0.3052	-0.3220	0.4554	0.0000	0.3108	0.1873	-0.2649	0.0000
3s'''	0.2137	-0.2371	0.3352	0.0000	-0.2237	-0.1726	0.2441	0.0000
3p _x	0.0001	-0.0001	0.0001	0.0000	-0.0254	-0.0250	0.0022	0.0000
3p _y	0.0000	0.0000	0.0000	-0.0001	0.0000	0.0000	0.0000	-0.0331
3p _z	-0.0001	0.0000	-0.0001	0.0000	0.0179	-0.0154	-0.0250	0.0000
3p _x	-0.0120	0.0018	0.0069	0.0000	0.7219	0.8124	-0.0356	0.0000
3p _y	0.0000	0.0000	0.0000	0.0095	0.0000	0.0000	0.0000	1.1133
3p _z	0.0085	0.0082	0.0018	0.0000	-0.5105	0.5389	0.8124	0.0000

a) The wavefunction has been computed using the symmetry of the D_{2h} subgroup of the tetrahedron.

all structures considered the stabilities are of the same order of magnitude as those obtained for the linear and triangular Mg_3 .

In particular, our investigation without the inclusion of d-orbitals in the AO basis set, confirms the results already reported in the literature on the tetrahedral Mg_4 cluster (172,193, 196) (Fig. 2.2.14a). In Table 2.2.15 are displayed the compositions of the valence MOs of Mg_4 (T_d). If we compare the coefficients of the expansion of the MOs in the basis of atomic orbitals with those of tetrahedral Be_4 (Table 2.2.6) for the same distance 4.0 a.u., we can note the negligible contribution of the 3p polarization functions to the a_1 and t_2 occupied MOs of Mg_4 . In other words, the s-p hybridization is not effective if the basis set does not contain d-functions.

Recently, Chiles et al. (198) have clearly shown that the total energy of the Mg_4 (T_d) cluster is largely influenced by the inclusion of one d-function in the AO basis set and that the binding is a consequence of electron correlation. The optimization of the geometry with the CEPA-2 method leads in fact to a considerable shortening of the bond distances and to an estimated stability of about 20 kcal/mole (198).

It is worth noting, moreover, that the matrix isolated Mg_4 cluster has been tentatively identified as a tetrahedral species (222).

We have performed some calculations for the $Mg_4(T_d)$ cluster

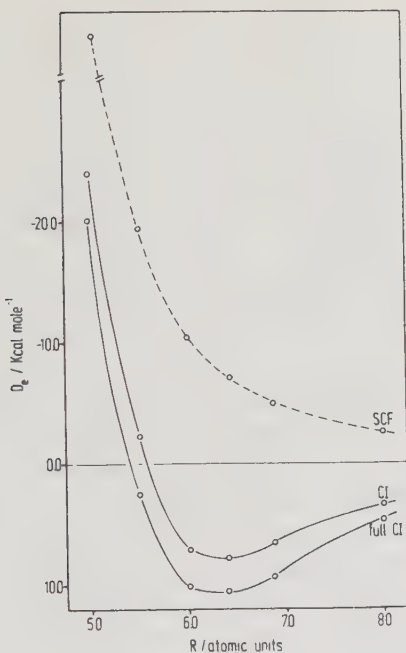


Fig. 2.2.15 - Potential energy curves for the 1A_1 ground state of tetrahedral Mg_4 computed with a basis set including d-functions.

adopting a more flexible basis set of the type $|4s2p1d|$ where the 3s orbital exponents are the same of Table 2.2.1, while 3p and 3d orbital exponents are those adopted by Chiles et al. (198) ($\alpha_p = 0.1324$, $\alpha'_p = 0.0413$, $\alpha_d = 0.14$). With this basis set the Mg_2 molecule is described as very weakly bonded species (the dissociation energy is smaller than 1 kcal/mole and the inter-nuclear separation larger than 10 a.u.). Moreover, the stability of Mg_2 is not too sensitive to the choice of the d-exponent.

At the SCF level the Mg_4 cluster is not bound (Fig. 2.2.15). On the contrary, the CI curve presents a minimum for the distance 6.4 a.u. with a D_e of 7.8 kcal/mole. The full CI estimate of the stability is of the order of 10 kcal/mole. In comparison with the calculation of Chiles et al. (198)

our value of D_e is smaller. This is not surprising if we consider the tendency of the CEPA-2 method to overestimate the strength of the bond in other Group IIa compounds (216,217).

The better description of the CI wave function with 7 reference configurations leads to a value of $D_e = 9.9$ kcal/mole, which is very close to the full CI estimate D_e (10.4 kcal/mole).

In comparison with the calculation performed without d-functions the totally symmetric $1a_1$ valence MO of Mg_4 is considerably lowered in energy, while the $1t_2$ HOMO (highest occupied MO) is shifted towards higher values. This change in the electronic structure is consistent with the relatively large D_e found when d-functions are used because the stability of tetrahedral alkaline-earth metal clusters largely depends on the nature and energy of the bonding a_1 valence MO, as shown in the case of Be_4 (see Fig. 2.2.6). Moreover, the inclusion of d-functions in the basis set stabilizes the LUMO (lowest unoccupied MO) of a_1 symmetry. The resulting smaller HOMO-LUMO energy difference can be considered as a measure of a rising metallic character. The singlet-triplet splitting computed at CI level for the equilibrium distance of the 1A_1 ground state of Mg_4 is 39 kcal/mole.

2.2.6.3 Mg_5

For the five-atom clusters we have studied, adopting the $|4s2p|$ basis set, the bipyramidal trigonal (D_{3h}), the square pyramidal (C_{4v}), the pentagon (D_{5h}) and a geometry (C_{2v}) derived as a part of the hcp Mg crystal lattice (Fig. 2.2.1).

The results parallel those found for the other, smaller Mg clusters considered (Table 2.2.14). The values of the IPs are found to be nearer to experimental atomic IP (7.6 eV) rather than to the electron work function of the metal (3.68 eV).

2.2.7 Ca_n clusters ($n = 3, 4, 5$)

Among the alkaline-earth clusters, Ca aggregates are supposed to be the most sensitive to the inclusion of d-polarization functions in the basis set. This is clearly shown, e.g., by the results obtained with the two $|4s2p|$ and $|4s2p1d|$ PP basis sets

Table 2.2.16 - Electronic properties of Ca clusters^{a)}

	Side bond length	E_{SCF} singlet	E_{SCF} triplet	$E_{\text{CI/BE}}$ singlet	$E_{\text{full CI/BE}}$ singlet	IP
$\text{Ca}_3(\text{D}_{3\text{h}})$	11.4	-1.8152	-1.7537	-1.8826/0.56	-1.8945/0.61	5.31
$\text{Ca}_3(\text{D}_{\infty\text{h}})$	12.1	-1.8154	-1.6949	-1.8822/0.29	-1.8940/0.32	5.32
$\text{Ca}_4(\text{T}_\text{d})$	10.1	-2.4198	-2.3431	-2.5072/1.83	-2.5245/1.98	5.12
$\text{Ca}_4(\text{D}_{4\text{h}})$	11.1	-2.4198	-2.3359	-2.5069/1.68	-2.5241/1.73	5.05
$\text{Ca}_4(\text{D}_{2\text{h}})$	11.3	-2.4197	-2.3246	-2.5058/0.94	-2.5231/1.05	5.13
$\text{Ca}_4(\text{D}_{\infty\text{h}})$	11.2	-2.4201	-2.3791	-2.5060/1.10	-2.5232/1.14	5.11
$\text{Ca}_5(\text{D}_{3\text{h}})$	10.2	-3.0246	-2.9666	-3.1299/2.82	-3.1531/3.27	4.85
$\text{Ca}_5(\text{C}_{4\text{v}})$	10.8	-3.0248	-2.9853	-3.1284/1.77	-3.1511/2.00	4.96
$\text{Ca}_5(\text{C}_{2\text{v}})$	11.2	-3.0250	-2.9847	-3.1276/1.32	-3.1503/1.51	5.08
$\text{Ca}_5(\text{D}_{5\text{h}})$	11.7	-3.0254	-2.9838	-3.1266/0.70	-3.1492/0.77	5.17

^{a)} All values are in au except the binding energies (BE) and the ionization potentials (IP) which are in kcal/mole and in eV respectively.

on Ca_2 (Table 2.2.3). Our investigation on larger aggregates has however been performed with the $|4s2p|$ basis set. In general, one may expect that the inclusion of d-functions gives smaller equilibrium bond lengths and larger dissociation energies compared to the value we obtain, as shown by the results on tetrahedral Ca_4 which has been computed also with the larger basis set.

2.2.7.1 Ca_3 -

The shapes of the potential energy curves for the $1^1_\text{g}^+$ and $3^3_\text{u}^+$ states of Ca_3 ($\text{D}_{\infty\text{h}}$) and for the 1^1A_1 and 3^3E states of Ca ($\text{D}_{3\text{h}}$) are very similar to those found for the corresponding Be and Mg aggregates.

The dissociation energies turn out to be larger than those of Mg_3 clusters, but still remain very small (Table 2.2.16). The minimum of the $3^3_\text{u}^+$ curve is only 25 kcal/mole above the limit of the three non-interacting atoms, and therefore the non-vertical energy gap between singlet and triplet states is intermediate between the Be_3 and Mg_3 clusters.

2.2.7.2 Ca_4 -

The electronic structure of tetrahedral Ca_4 has been studied by Stoll et al. (172) using a PP method combined with a density functional approximation of the correlation energy.

Table 2.2.17 - Orbital energies and coefficients of the valence molecular orbitals of tetrahedral Ca_4 ^{a)}

	1a ₁	1t ₂	1t ₂	1t ₂	2a ₁	2t ₂	2t ₂	2t ₂
orbital energy (au)	-0.23975	-0.18362	-0.18362	-0.18362	0.00812	0.02302	0.02302	0.02302
4s	-0.0062	0.0076	-0.0108	0.0000	-0.0044	0.0014	0.0020	0.0000
4s'	-0.1030	0.1161	-0.1642	0.0000	-0.0007	0.0213	0.0301	0.0000
4s''	0.3083	-0.3406	0.4816	0.0000	-0.0788	-0.0710	-0.1004	0.0000
4s'''	0.1599	-0.2714	0.3838	0.0000	0.2248	-0.0453	-0.0640	0.0000
4p _x	0.0042	-0.0022	-0.0015	0.0000	-0.0321	0.0397	0.0091	0.0000
4p _y	0.0000	0.0000	0.0000	-0.0047	0.0000	0.0000	0.0000	-0.0471
4p _z	-0.0029	-0.0031	-0.0022	0.0000	0.0227	0.0190	-0.0397	0.0000
4p _x '	-0.0611	0.0371	0.0234	0.0000	0.6737	-0.8095	-0.1852	0.0000
4p _y '	0.0000	0.0000	0.0000	0.0758	0.0000	0.0000	0.0000	0.9596
4p _z '	0.0432	0.0496	0.0371	0.0000	-0.4764	-0.3872	-0.8094	0.0000

a) The wavefunction has been computed using the symmetry of the D_{2h} subgroup of the tetrahedron.

The conclusions reached by these authors are in qualitative agreement with the present results (if d-functions are not considered), which predict a binding energy of 1.8 kcal/mole for an equilibrium distance of 10.1 a.u. (Table 2.2.16 and Fig. 2.2.14b). The larger involvement of p-functions in the MOs of tetrahedral Ca_4 with respect to the corresponding Mg cluster (Table 2.2.15 and 2.2.17) is responsible for the slightly higher stability observed.

The same is true also for the other considered Ca_4 clusters, namely square, rhombus and linear, whose dissociation energies are always larger than in the corresponding Mg aggregates (see Table 2.2.14 and 2.2.16).

As for tetrahedral Mg_4 , also in the case of Ca_4 (T_d) a more careful analysis of the electronic structure has been done adopting a larger PP basis set, $|4s2p1d|$. The 4s orbital exponents are the same of the Table 2.2.1 while the polarization functions have been optimized at molecular level ($\alpha_p = 0.54$, $\alpha_p' = 0.0705$, $\alpha_d = 0.132$). With this basis set we found a CI D_e of 11 kcal/mole for the equilibrium bond length of 8.1 a.u. (13.9 kcal/mole in full CI) (Fig. 2.2.16). However, differently from tetrahedral Mg_4 , a very weak attractive interaction is observed also in the SCF curve (compare Fig. 2.2.15 and 2.2.16).

The same considerations about the electronic structure of Mg_4 are valid also for Ca_4 . In particular, with respect to the

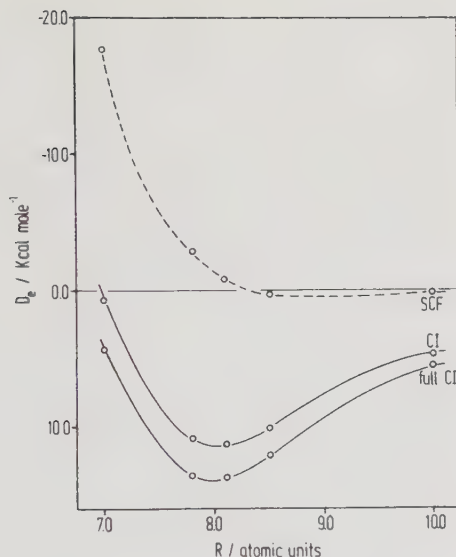


Fig. 2.2.16 - Potential energy curves for the 1A_1 ground state of tetrahedral Ca_4 computed with a basis set including d-polarization functions.

calculation without d-functions, the $1a_1$ valence MO is stabilized and the $1t_2$ MOs are shifted to higher values. The HOMO-LUMO energy difference is reduced and the computed singlet-triplet excitation energy of Ca_4 computed in the minimum of the singlet potential energy curve is 20 kcal/mole.

2.2.7.3 Ca_5

Among the Ca_5 clusters here considered adopting the $|4s2p|$ basis set, the bipyramidal trigonal (D_{3h}) is the most stable geometry, with a D_e of 2.8 kcal/mole. The corresponding binding energy per atom, 0.56 kcal/mole, is larger than that of tetrahedron (0.46 kcal/mole), following the trend already observed for Be and Mg clusters. A small stability is also shown by the square pyramidal and by the C_{2v} structures, while the pentagon is the least favoured Ca_5 cluster.

2.2.8 Discussion

The PP MRD CI potential energy curves for the symmetrical approach of atoms forming the Be clusters $\text{Be}_4(\text{T}_d)$, $\text{Be}_5(\text{D}_{3h})$, $\text{Be}_5(\text{D}_{5h})$ and $\text{Be}_5(\text{C}_{4v})$ (Fig. 2.2.4) exhibit a deep minimum due to the s-p hybridization. The depth of this minimum largely depends on the geometry of the cluster while the internuclear separation is practically the same and is very close to the Be-Be distance present in the crystal (about 4.2 a.u.). This inner minimum is separated from the second shallow minimum (at distances of about 9 a.u.) by a maximum or a saddle point on the energy hypersurface. For some particular structures, such as square or rhombus, there is no evidence of the formation of s-p hybrids and the inner deeper minimum disappears, giving rise to a very weakly bonded species. On the contrary, structures which can be considered as sections of the hcp crystal lattice, with atoms in a tetrahedral coordinative position (e.g. $\text{Be}_4(\text{T}_d)$, $\text{Be}_5(\text{D}_{3h})$, $\text{Be}_6(\text{D}_{2h})$) or in larger planar arrangements are very stable because of the uniform participation of the p-orbitals to the bond.

It is important to note that not only the number of bonds per atom in the cluster, but also the number of atoms having non-optimal direction of the bonds formed with the nearest neighbors plays an important role.

The CI procedure is essential for the exact determination of the electronic structure of Be clusters. The molecular ground state is different in SCF and CI procedures for many Be clusters. Already in Be_7 the energies of some states are separated only by few kcal/mole. Therefore it is not surprising that the relative positions of some of these states are reversed after inclusion of correlation effects.

The separation between the lowest singlet and lowest triplet electronic states decreases with the increasing cluster size. The existence of energetically low-lying triplet states is probably connected with the increasing metallic character and cannot be attributed to "edge" or "corner" effects in a simple way. For symmetrical clusters the open shell MOs are delocalized over many atomic centers not necessarily located at the periphery of the

cluster. The frontier orbitals are either not localized or exhibit a special character along the whole cluster periphery. If the existence of energetically very low-lying triplets is due to the existence of the cluster borderies then this phenomenon does not disappear with the increasing size of the cluster.

Planar and non-planar Be clusters exhibit comparable atomization energies and, on the basis of the present calculations, it is not possible to decide which structures are energetically more favoured. In planar Be clusters the p_z orbitals contribute to the stability through a bonding combination of π character, but the cluster stability is mainly due to the strong in-plane p_σ bonds. For non-planar structures the bonding between layers causes a depletion of electrons from the in-plane p_x and p_y orbitals to the p_z orbitals. The considerable stability found for relatively large planar arrangements of Be atoms agrees with some recently performed quantum-mechanical ab initio calculations on Be monolayers (226). The experimental evidence obtained by LEED measurements (227,228) that the (0001) surface of Be does not reconstruct can be related to the intrinsic stability of planar sections of the hcp Be crystal lattice.

The general trend of increasing binding energy per atom with increasing cluster size demonstrates that the order of magnitude of the experimental heat of sublimation of the Be bulk (12.8 kcal/mole (229)) can be explained with the general kind of binding which is already present in Be clusters.

On the other hand, for the Mg and Ca clusters the situation looks quite different from that found for the bonded Be clusters. When basis sets do not contain d-polarization functions the respective potential energy curves always show a very shallow minimum at larger distances. This situation is completely changed by the inclusion of d-functions in the AO basis set. In this case in fact, both Mg_4 and Ca_4 clusters in a tetrahedral geometry are bonded although the whole stability is small if compared with that of the corresponding Be_4 cluster.

In contrast to Be, the kind of bonding in Mg and Ca clusters suggests that strong changes in the nature of the bond should take place in larger agglomerates.

2.3 ALUMINIUM CLUSTERS [#]

2.3.1 Introduction

Despite the technical importance of aluminium, very few experiments on Al clusters of small size have been reported in the literature. Aluminium clusters of small size (1-13 atoms) have been detected with quadrupole mass spectrometry in Al cluster beams (230) and the optical spectra of matrix isolated Al and Al₂ have been recently reported (78).

However, no experimental information is available on cluster geometry, ionization potential, electronic structure, etc.

Aluminium clusters have been theoretically studied, but not in a systematic way. Schwartz and Quinn (139,231) have reported some SCF results on the interaction of Al clusters with the oxygen atom. A similar problem has been investigated by Cox and Bauschlicher (138). They have performed Hartree-Fock calculations on the chemisorption of O, Li and Na on a cluster of 19 Al atoms representing the Al (111) surface. The only previous ab initio calculation on naked Al clusters is that of Bauschlicher et al. (232) on Al₁₀(7,3) and Al₁₃(4,5,4), where the number in parenthesis indicate the number of Al atoms in each layer. In this study it was found that the formation of Al-Al bonds leads to a 3s to 3p promotion in the Al atoms corresponding to a substantial sp hybridization. Moreover, the electronic distribution on some atoms dramatically depends on the number and on the position of the nearest neighbors. Therefore, the choice of a finite Al cluster to model chemisorption processes requires some care (232).

2.3.2 Computational details and basis set specification

The calculations reported in this chapter have been performed with the |4s4p/2s2p| PP valence basis set adopted for the study of the Al₂ molecule (see Section 1.2.4.3).

The effect of d-functions is expected to be large and there-

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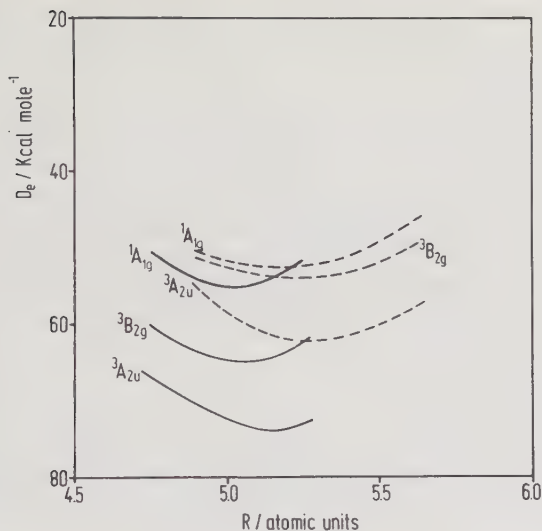


Fig. 2.3.1 - Potential energy curves for the lowest-lying states of square Al_4 computed adopting a basis set with (—) and without (---) d-polarization functions.

fore has been tested in the determination of the potential energy curves for the low-lying states of square and rhombic Al_4 . The d-exponent has been optimized on the Al_2 molecule (Section 1.2.4.3). The results for square and rhombic Al_4 (with the angle of 120 degrees) are reported in Fig. 2.3.1 and 2.3.2, respectively)

The influence of d-functions on the ordering and on the dissociation energies of the different states is not too large. On the contrary, the d-polarization functions have a dramatic influence on the determination of the equilibrium bond lengths and on the vibrational frequencies.

However, a vibrational analysis of Al clusters beyond of the scope of this study and we believe that for our qualitative purposes the basis set without d-functions can provide general information on the nature of the chemical bonding in small aluminium clusters.

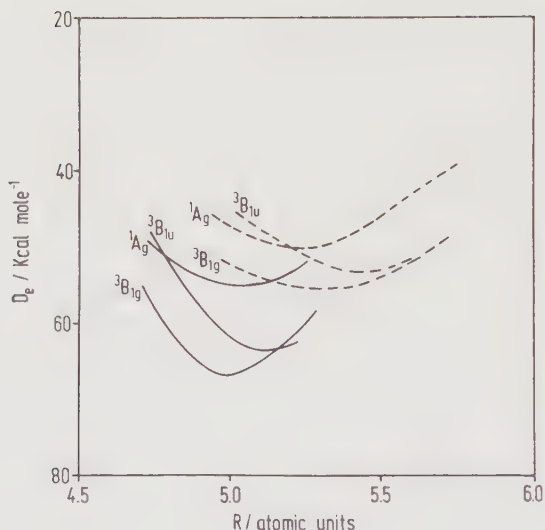


Fig. 2.3.2 - Potential energy curves for the lowest-lying states of rhombic Al_4 with the angle of 120 degrees computed adopting a basis set with (—) and without (---) d-polarization functions.

2.3.3 Al_3 , Al_4 and Al_5 clusters

Linear and equilateral triangle Al_3 clusters display comparable stabilities and have quadruplet ground states (but the quadruplet state of the D_{3h} cluster is nearly degenerate with the doublet state, $\Delta E = 1$ kcal/mole). The deformation of the linear structure to give the triangular one occurs without any appreciable change in energy and probably no energy barriers are to be expected in this process. Similarly, the potential energy curves for the geometrical deformation from square to rhombic Al_4 are very flat (Fig. 2.3.3) and the difference in stability of the two forms is of the same order of magnitude as their zero-point vibrational energies.

The change in geometry from D_{2h} to D_{4h} is not accompanied by drastic changes in the electronic structure. The valence electronic configuration corresponding to the $3B_{1u}$ ground state of rhombic Al_4 is $(1a_g)^2(1b_{2u})^2(1b_{3u})^2(2a_g)^2(1b_{1g})^2(1b_{1u})^1(3a_g)^1$.

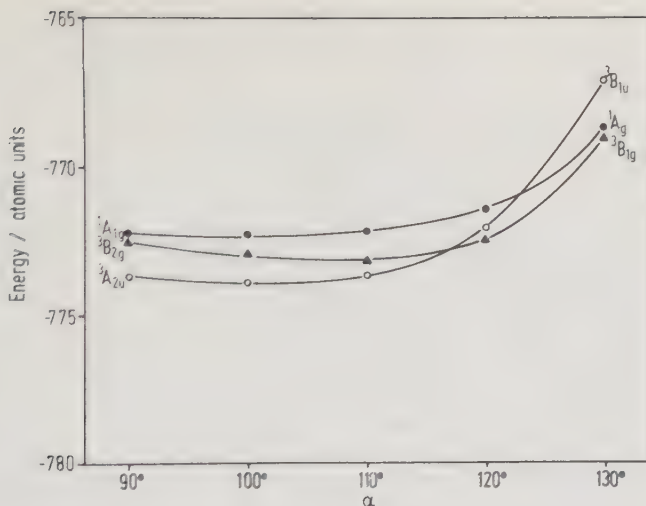


Fig. 2.3.3 - Potential energy curves for the process $\text{Al}_4(\text{D}_{4h}) \rightarrow \text{Al}_4(\text{D}_{2h})$. The Al-Al bond distance has been fixed to 5.25 a.u. .

With the change of the internal angle from 120 to 90 degrees the $1b_{2u}$ and $1b_{3u}$ MOs transform into the degenerate $1e_u$ MOs of D_{4h} symmetry and the b_{1g} and b_{1u} MOs of D_{2h} into the b_{2g} and a_{2u} MOs of D_{4h} , respectively (Fig. 2.3.4). The occupation of these MOs does not change with the geometrical modification and the $^3A_{2u}$ ground state of square Al_4 has the electronic configuration $(1a_{1g})^2(1e_u)^4(1b_{1g})^2(1b_{2g})^2(1a_{2u})^1(2a_{1g})^1$. An interesting characteristic of square and rhombus Al_4 is the existence of two energetically separated sets of MOs mainly composed of 3s and 3p atomic orbitals, respectively.

In rhombic Al_4 , e.g., the combination of 3s Al orbitals generates the completely filled pairs of bonding and antibonding $1a_g$, $2a_g$ and $1b_{2u}$, $1b_{3u}$ MOs. The stability of the cluster is largely due to the overlap between 3p atomic orbitals which combine to generate a set of energetically close lying MOs.

The number of valence electrons however is not sufficient to fill all these MOs with "p" character and the energy necessa-

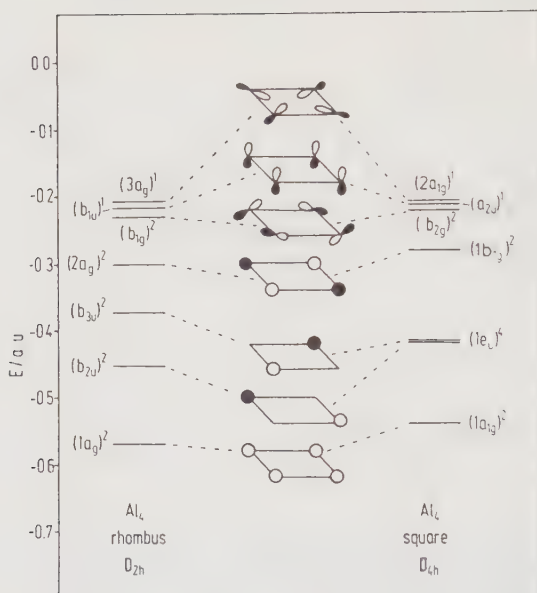


Fig. 2.3.4 - Molecular orbital scheme for rhombic and square Al_4 clusters

ry to couple the spins exceeds the energy separation between these levels. The $^1\text{A}_g$ state, where the $1b_{1u}$ MO is doubly occupied and the $3a_g$ MO is virtual, is in fact about 10 kcal/mole less stable than the $^3\text{B}_{1u}$ ground state (Fig. 2.3.3).

The tendency to have high spin multiplicities (triplet or quadruplet) is a general characteristic which can be found for other Al clusters (Table 2.3.1). For example, the other considered Al tetramers, tetrahedron and T-form, which show a binding energy per atom smaller than that of the D_{2h} and D_{4h} clusters, have both a triplet ground state as well (Table 2.3.1).

The deformability of Al_3 , Al_4 and Al_5 clusters (the two investigated Al pentamers, trigonal bipyramid and square pyramidal, have comparable stabilities and quadruplet ground states, see Table 2.3.1) can be considered a general characteristic of small Al clusters.

Table 2.3.1 - Electronic properties of Al clusters

cluster	ground ^{a)} state	theoretical ^{b)} treatment nM/ $\sum_i c_i^2$	r_e (a.u.)	E_{corr} (a.u.)	E_{CI} (a.u.)	BE/n (kcal/mol)
Al ₃ linear	q	3M/ .85	5.16	.0956	-5.7936	13.6
Al ₃ equilateral triangle	q	3M/ .87	5.51	.0997	-5.7924	13.4
Al ₄ rhombus ^{c)}	t	3M/ .84	5.24	.1516	-7.7380	15.8
Al ₄ square	t	3M/ .83	5.35	.1517	-7.7378	15.5
Al ₄ T-form	t	3M/ .83	5.33	.1371	-7.7221	13.2
Al ₄ tetra- hedron	t	3M/ .84	5.67	.1528	-7.7177	12.4
Al ₅ square pyramidal	q	3M/ .83	5.67	.1731	-9.6628	14.4
Al ₅ bipyramidal trigonal	q	3M/ .85	5.71	.1743	-9.6609	14.1

a) q = quadruplet, t = triplet.

b) nM indicates the number of reference configurations from which all single and double excitations are generated. All configurations which contribute more than 1 per cent to the CI expansion are chosen as leading configurations. $\sum_i c_i^2$ gives the total weight of the main configurations in the final CI wave function.

c) The optimized angle of the rhombus is 100°.

The computed equilibrium bond lengths are dispersed into the range 5.2-5.7 a.u. depending on the geometry and on the spin multiplicity of the cluster. These values are not too different from the Al-Al distance present in metallic aluminium which crystallizes in a fcc structure with a nearest neighbor distance of 5.41 a.u. .

In addition to the above mentioned properties of Al clusters, that is deformability and preference for high spin-multiplicity ground states, two other general features must be emphasized: 1) most stable Al clusters have structures which are sections of the fcc crystal lattice and 2) the data of population analysis indicate that the formation of the bonds in the cluster causes a sp hybridization which increases the trivalent character of the metal atom.

2.4 GERMANIUM CLUSTERS

2.4.1 Introduction

Among clusters of elements of Group IVA, small size Ge clusters have been experimentally investigated by different authors. The first experiment on Ge clusters was done in 1954 (233,234) but more recent investigations have been reported. In the experiment of Kant and Strauss (235) pure germanium was vaporized in a Knudsen cell and the resultant molecular species analyzed in a time-of-flight mass spectrometer. In this way the atomization energies of small Ge clusters were determined (235). With a slightly modified technique Kingcade et al. (236) have recently determined with greater accuracy the stabilities of Ge_2 , Ge_3 and Ge_4 .

All these studies provide some insight into the question of the stability of these clusters, but very few is known about their structures and properties.

While a quite large number of structural data is available on the anionic clusters of the isovalent tin and lead atoms (Sn_5^- , Sn_9^{4-} , Pb_5^{2-} , Pb_7^{4-}) the only Ge_n species isolated in solid state and characterized by X-ray crystallography are Ge_9^{2-} and Ge_9^{4-} (237). These two species are present in the cluster compound $|\text{crypt-K}^+|_6 \text{Ge}_9^{2-} \text{Ge}_9^{4-} \cdot 2.5 \text{ en}$ and the respective geometries are a tricapped trigonal prism of D_{3h} symmetry and a monocapped square antiprism of C_{4v} symmetry, respectively (237).

Theoretical investigations of Ge clusters do not seem to exist up to date.

2.4.2 Computational details and basis set specification

The Ge atom has the electronic configuration $|\text{Ar}| 3d^{10} 4s^2 4p^2$. The inclusion of the 3d electrons in the core of the atom might be questionable. However, the Roothan-Hartree-Fock atomic wave function (112) gives a separation of 1.08 a.u. (Table 2.4.1) for the two energy levels 3d-4s of Ge, so that the inclusion of 3d electrons in the core seems to be acceptable.

The pseudopotential parameters have been obtained from the

Table 2.4.1 - Atomic orbital energies in a.u. for the Ge ground state (3P)

	RHF†	PP
$3d^{10}$	-1.63475	—
$4s^2$	-0.55331	-0.54456
$4p^2$	-0.28729	-0.28169

† Roothan-Hartree-Fock wavefunction [142]

$4s^2 4p^2$ (3P) ground state of Ge for the s and p components, and from the $4s^2 4p 4d$ (3D) excited atomic state for the d component (111). The PP atomic basis set for Ge ground state, consisting from 4s and 4p primitive Gaussian functions, has been previously optimized (117). With this basis set the energy values of the 4s and 4p atomic orbitals are well reproduced in the PP scheme although the 3d electrons are not explicitly included in the calculation (Table 2.4.1).

The first basis set adopted for the molecular calculations, denoted as basis set I, has been obtained by contraction of the two inner s and p Gaussian functions. This basis set $|4s4p/3s3p|$ is of triple-zeta quality concerning the valence electrons and it is sufficiently flexible in order to avoid the occurrence of

Table 2.4.2 - Atomic basis set for Ge; the 4s and 4p exponents have been taken from Ref. (117).

Orbital	Exponent/ a_0^{-2}	Contraction coefficient
4s	4.215430	-0.013778
	1.218550	-0.222145
	0.226232	1
	0.083741	1
4p	2.329990	-0.031578
	0.306352	0.361943
	0.120077	1
	0.047198	1
4d	0.231240	1
	0.12	1

basis set superposition errors. The counterpoise correction to the computed SCF dissociation energy of Ge_2 is in fact only 0.03 kcal/mole.

For clusters containing more than five atoms a double-zeta contraction scheme $|4s4p/2s2p|$ has been adopted. The SCF results are practically insensitive to the different contraction schemes whereas the CI binding energies are slightly larger when computed with the $|4s4p/3s3p|$ basis set.

For the Ge_2 molecule a second set of calculations has been performed with the $|4s4p1d/3s3p1d|$ basis set II which includes one d-polarization function. The 4d exponent was optimized at molecular level for the Ge_2 system. A basis set including a second diffuse d-function was adopted for the evaluation of the dissociation energy of Ge_2 (basis set III, $|4s4p2d/3s3p2d|$). The exponents and contraction coefficients used are given in Table 2.4.2.

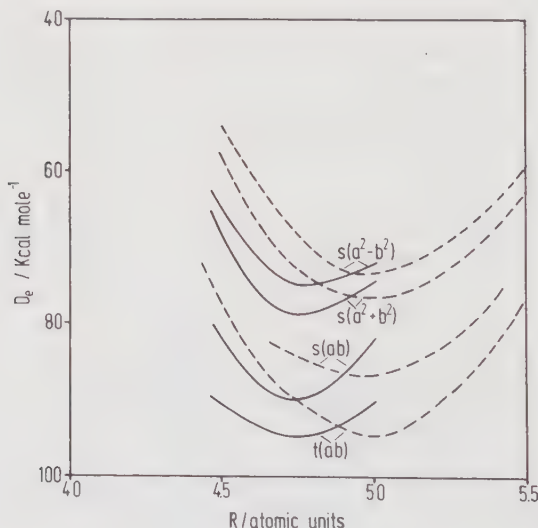


Fig. 2.4.1 - Potential energy curves for the low-lying states of square Ge_4 computed with (—) and without (---) d-polarization functions.

The effect of the inclusion of one d-polarization function in the AO basis set has been considered also for square and rhombic Ge_4 . The potential energy curves for the low-lying states of these two clusters obtained with and without d-functions are compared in Fig. 2.4.1 and Fig. 2.4.2, respectively.

Even if the total energy of the system is appreciably lowered when d-functions are considered, the dissociation energy of the cluster remains unchanged in the case of square Ge_4 and increases of about 10 per cent for rhombic Ge_4 .

More pronounced is the influence of d-functions on the determination of the equilibrium bond lengths. The minima of the curves of both Ge_4 clusters are shifted towards smaller values

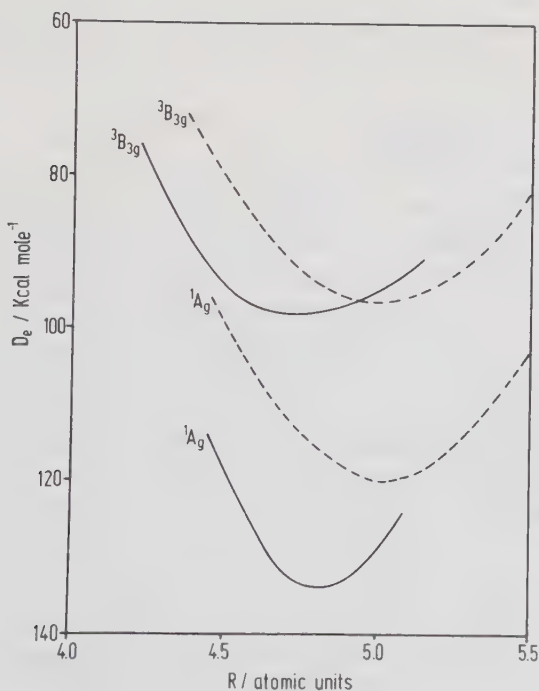


Fig. 2.4.2 - Potential energy curves for the low-lying states of rhombic Ge_4 computed adopting a basis set with (—) and without (---) d-polarization functions.

when d-functions are considered. The role of d-functions can be considered important but not crucial for the description of the chemical bonding in Ge clusters.

Therefore, the curves for the lowest singlet, triplet and quintuplet state of each Ge cluster considered have been determined adopting the basis set I previously described. The optimization of the interatomic distances in CI has been performed using in general only one main configuration (1M) but the final CI energy for the minimum geometry has been computed with three or more main configurations.

The dimensions of the secular problem range from 3000 to 5800 configurations, while the CI energy was extrapolated to the whole CI space of dimension varying from 20 000 to 150 000 configurations, depending on the size of the cluster and on the details of the calculation.

2.4.3 The Ge_2 molecule*

The first study on the stability of Ge_2 dates from 1954 (233) but the dissociation energy (D_e) for the process $\text{Ge}_2 (\text{gas}) \rightarrow 2 \text{Ge} (\text{gas})$ has been evaluated also recently (235,236). Therefore it is quite surprising that no spectroscopical investigations have been reported up today on this molecule and that no experimental information is available about ground state, spin multiplicity, equilibrium bond distance and electronic structure of Ge_2 .

On the other hand, the study of Ge_2 can provide some insight into similarities and differences among dimers of Group IVA, in particular C_2 , Si_2 and Ge_2 .

The question if the true ground state of the C_2 molecule is the $^1\Sigma_g^+$ ($\pi_u^4 \sigma_g^0$) or the $^3\Pi_u$ ($\pi_u^3 \sigma_g^1$) has been the subject of many discussions in the past (142). In 1963 Ballik and Ramsey (238) have found that the $^1\Sigma_g^+$ is actually the ground state which is separated from the upper $^3\Pi_u$ state by only 716 cm^{-1} .

On the contrary, the experimentally observed ground state

* The present section 2.4.3 has been partly published in the paper /6/ of the list of p. 201 .

of Si_2 is a $^3\Sigma_g^-$ (239), which has been recently confirmed by some theoretical investigations (240-242).

Whether the ground state of Ge_2 is the $^1\Sigma_g^+$ as in the case of C_2 or the $^3\Sigma_g^-$ as in the case of Si_2 is not trivial to determine although some theoretical results obtained employing different levels of theory (243,244) suggest a qualitative similarity between the electronic structures of Ge_2 and Si_2 .

2.4.3.1 Ge_2 potential energy curves

The interaction of two Ge atoms in their respective atomic ground states (^3P) gives rise to 18 possible molecular electronic states (Table 2.4.3). Among them, we have considered the four low-lying singlet states, $1^1\Sigma_g^+$, $2^1\Sigma_g^+$, $1^1\Pi_u$, and $1^1\Delta_g$, the two lowest triplet states $^3\Sigma_g^-$ and $^3\Pi_u$, and the lowest quintuplet, $^5\Pi_g$.

The potential energy curves computed at CI level with the basis sets I and II are given in Fig. 2.4.3 and Fig. 2.4.4, respectively. Comparing these curves it is evident that the basis set I is inadequate for the determination of the ground state of the molecule. The two $^3\Pi_u$ and $^3\Sigma_g^-$ states are in fact close lying but their ordering is reversed when the basis set II is adopted.

In contrast, both the SCF procedures employing the basis set I and II yield for the ground state the $^3\Sigma_g^-$ state corresponding to the valence electronic configuration $1\sigma_g^2 1\sigma_u^2 1\pi_u^2 2\sigma_g^2$. The similarity of both SCF treatments can also be deduced from the curves of Fig. 2.4.5, in which the energies of the occupied MOs and of the LUMO for the $^3\Sigma_g^-$ ground state are given as function of the interatomic distance.

Table 2.4.3 - Molecular states of Ge_2 arising from $^3\text{P} + ^3\text{P}$ atomic terms.

Singlets	$^1\Sigma_g^+(2)$, $^1\Pi_u$, $^1\Delta_g$, $^1\Sigma_u^-$, $^1\Pi_g$
Triplets	$^3\Sigma_g^-$, $^3\Pi_u$, $^3\Sigma_u^+(2)$, $^3\Pi_g$, $^3\Delta_u$
Quintuplets	$^5\Pi_g$, $^5\Sigma_g^+(2)$, $^5\Sigma_u^-$, $^5\Pi_u$, $^5\Delta_g$

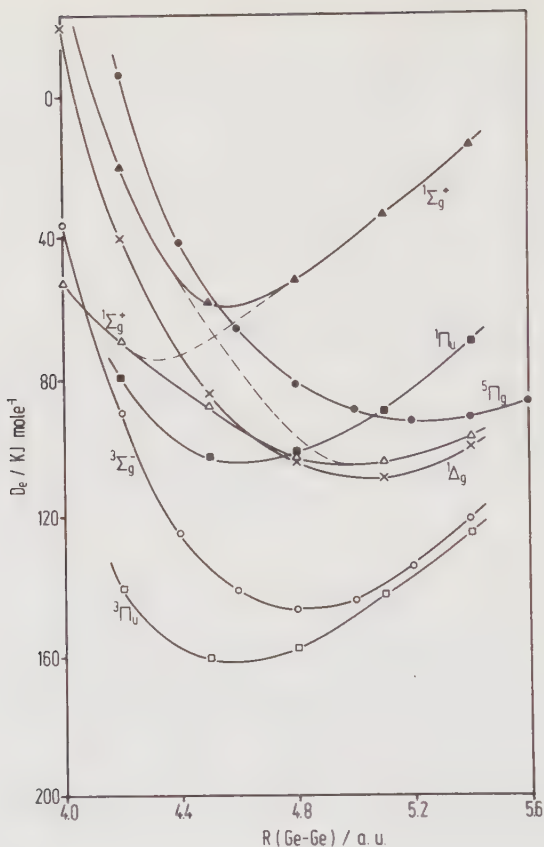


Fig. 2.4.3 - Potential energy curves for the low-lying states of Ge_2 (basis set I). The dotted lines indicate the avoided crossing between the two $1\Sigma_g^+$ states. The details of the MRD CI treatment are given in Table 2.4.4 .

The available literature data on the ground state of Ge_2 are controversial . The Extended-Hückel calculation of Anderson (243) predicts the $3\Pi_{u-1}$ to be the ground state of Ge_2 and the $3\Sigma_g^-$ to lie only 1049 cm^{-1} above the $3\Pi_u$. On the contrary, Harris and Jones (244) found, with a pseudopotential method combined with

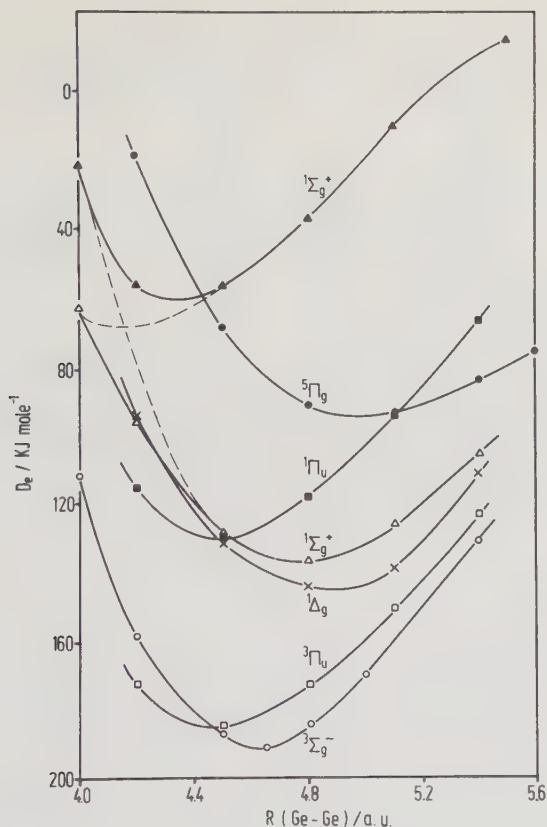


Fig. 2.4.4 - Potential energy curves for the low-lying electronic states of Ge_2 (basis set II). The dotted lines indicate the avoided crossing between the two $1\Sigma_g^+$ states. The details of the MRD CI treatment are given in Table 2.4.5.

a density-functional formalism, that the $3\Sigma_g^-$ is the ground state and that the energy separation from the upper $3\Pi_u$ state is of 3458 cm^{-1} . Finally, in the X_α calculation of Gadiyak et al. (245) the $\pi_u^2\sigma_g^2$ configuration was assumed as the molecular ground state.

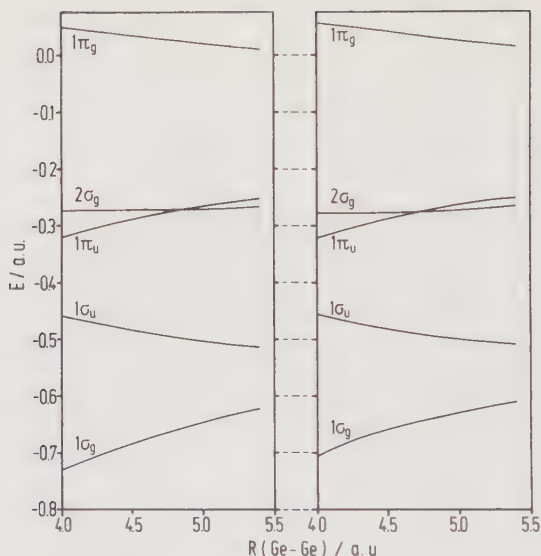


Fig. 2.4.5 - MO energy levels as function of the internuclear separation. Left-side basis set I, right-side basis set II.

Our finding that the ${}^3\Sigma_g^-$ and ${}^3\Pi_u$ states are almost degenerated (the transition energy T_e is 501 cm^{-1} as computed with the basis set II) contrasts the results of Harris and Jones (244). However, our result is not completely unexpected knowing that the energy separation of these two states in Si_2 is even smaller. The computed value of T_e for these two states obtained from the large scale MRD CI calculation is in fact 161 cm^{-1} (240,241).

The curves obtained with basis set II (Fig. 2.4.4) show a crossing of the two states ${}^3\Sigma_g^-$ and ${}^3\Pi_u$ at the distance 4.47 a.u., so that for shorter distances the ${}^3\Pi_u$ is effectively the ground state of the molecule. Except for these two nearly degenerate triplet states, the energy ordering of the higher excited states of Ge_2 computed with basis set I and II is identical. However,

Table 2.4.4 - Computed spectroscopic constants for some low-lying states of Ge_2 (basis set I).

State	T_e/cm^{-1}	R_e/a_0	k/Nm^{-1}	ω_e/cm^{-1}
$^3\Pi_u (\pi u^3 \sigma_g^1)$	0	4.618	63.1	172
$^3\Sigma_g^- (\pi u^3 \sigma_g^3)$	1240	4.837	59.7	167
$^1\Delta_g (\pi u^3 \sigma_g^2)$	4375	5.061	47.0	148
$^1\Sigma_g^+ (\pi u^4 \sigma_g^0)$	4674	5.014	36.3	130
$^1\Pi_u (\pi u^3 \sigma_g^1)$	4734	4.656	64.0	173
$^3\Pi_g (\sigma_g^1 \pi u^3 \pi_g^1)$	5717	5.247	35.5	129
$^1\Sigma_g^+ (\pi u^2 \sigma_g^3)$	8534	4.615	128.4	245

T_e =transition energy, R_e =equilibrium bond length, k =force constant, ω_e =vibrational frequency. The CI treatment adopted is of the type $3M/1R$, $1M/1R$, $2M/1R$, $4M/2R$, $3M/1R$, $1M/1R$, for the $^3\Pi_u$, $^3\Sigma_g^-$, $^1\Delta_g$, $^1\Sigma_g^+$ (2), $^1\Pi_u$, $^3\Pi_g$ states, respectively. The values of $\sum_i c_i^2$ (see text for definition) are 0.92, 0.91, 0.91, 0.92,

0.91, 0.91, 0.92, respectively. The $^3\Sigma_g^-$ SCF MOs have been employed for the MRD CI treatment of the singlet states.

in general the basis set II shows the tendency to yield larger values of the transition energies and of the vibrational frequencies and shorter equilibrium bond lengths than the basis set I (Table 2.4.4 and Table 2.4.5).

The lowest singlet state, $^1\Delta_g$, is fairly close in energy to the other two singlet states, $^1\Sigma_g^+$ and $^1\Pi_u$. These are followed by the first quintuplet state, $^5\Pi_g$ and by a second singlet of Σ_g symmetry. An avoided crossing between the two $^1\Sigma_g^+$ states is due to the change in contribution of configurations $\pi_u^2 \sigma_g^2$ and $\pi_u^4 \sigma_g^0$. The former one has larger weight at shorter distances and the latter is dominant at larger internuclear separations.

The analogies between the curves of Fig. 2.4.4 and those reported in ref. (240,241) for Si_2 are striking. Not only the almost degeneracy of the two lowest $^3\Sigma_g^-$ and $^3\Pi_u$ states but even the ordering and the shapes of the first excited states are very similar for the two dimers. Apart from the reversal of the two close lying states $^1\Pi_u$ and $^1\Sigma_g^+$, the vertical excitation energies are of the same order of magnitude in both molecules (compare the values of Table 2.4.5 with the values of T_e for Si_2 which are 161, 3871, 4436 and 5646 cm^{-1} for the transitions from the ground to

Table 2.4.5 - Computed spectroscopic constants for some low-lying states of Ge_2 (basis set II).

State	T_e/cm^{-1}	R_e/a_0	k/Nm^{-1}	ω_e/cm^{-1}
$^3\Sigma_g^- (\pi_u^2 \sigma_g^2)$	0	4.631	111.6	228
$^3\Pi_u (\pi_u^3 \sigma_g^1)$	501	4.504	81.1	195
$^1\Delta_g (\pi_u^2 \sigma_g^2)$	3871	4.865	57.9	165
$^1\Sigma_g^+ (\pi_u^4 \sigma_g^0)$	4597	4.773	58.8	166
$^1\Pi_u (\pi_u^3 \sigma_g^1)$	5166	4.514	84.4	199
$^3\Pi_g (\sigma_g^1 \pi_u^2 \pi_g^1)$	8090	5.020	52.0	156
$^1\Sigma_g^+ (\pi_u^2 \sigma_g^2)$	10969	4.355	103.8	220

T_e =transition energy, R_e =equilibrium bond length, k =force constant, ω_e =vibrational frequency. The CI treatment adopted is of the type $1M/1R$, $3M/1R$, $2M/1R$, $4M/2R$, $3M/1R$, $1M/1R$ for the $^3\Sigma_g^-$, $^3\Pi_u$, $^1\Delta_g$, $^1\Sigma_g^+$ (2), $^1\Pi_u$, $^3\Pi_g$ states, respectively. The values of $\sum_i c_i^2$ (see text for definition) are 0.88, 0.88, 0.88, 0.88,

0.88, 0.84, 0.88 and 0.89, respectively. The $^3\Sigma_g^-$ SCF MOs have been employed for the MRD CI treatment of the singlet states.

the $^3\Pi_u$, $^1\Delta_g$, $^1\Pi_u$, and $^1\Sigma_g^+$ excited states, respectively (240, 241). The equilibrium bond lengths of Ge_2 are only slightly larger than in the case of Si_2 . The larger value of the reduced mass of Ge gives rise to smaller vibrational frequencies, but the shape of the curves around the minimum region are very similar so that the force constants of Ge_2 are comparable with those of Si_2 (244).

The dissociation energy has been experimentally measured by mass spectrometry. The values of D_e determined in this way by different authors are 64.1 ± 5 (246), 65.1 ± 5 (235), 64.6 ± 5 (247), and 61.2 ± 2 (236) kcal/mole.

The dissociation energies obtained with basis set I, II and III are given in Table 2.4.6 and are compared with the theoretical results of other authors. From these data it is evident that the SCF procedure is not able to reproduce more than about 40 per cent of the experimental D_e , even when basis set III including two d-polarization functions is employed.

The inclusion of correlation effects in the theoretical treatment improves the agreement with the experimental data, but even the full CI value of D_e obtained with the basis set III yields

Table 2.4.6 - Dissociation energies of Ge_2 as obtained with different levels of theoretical treatment (energies in kJ/mole) .

Present work			
	Basis set I	Basis set II	Basis set III†
Ground state (CI)	$^3\Pi_u$	$^3\Sigma_g^-$	$^3\Sigma_g^-$
D_e (SCF)	34.3‡	108.7	116.8
D_e (CI)	162.2	197.2	207.9
D_e (full CI)	176.1	205.6	225.5
	Anderson [243]	Harris and Jones [244]	Experimental [236]
Ground state	$^3\Pi_u$	$^3\Sigma_g^-$	—
D_e	238.3	192.8	255.7 ± 10

† The calculation has been performed for the minimum distance obtained with basis set II.

‡ The SCF ground state is $^3\Sigma_g^-$.

only 85-88 per cent of the measured stability (Table 2.4.6). It is possible to speculate that with the inclusion of polarization functions of higher angular momentum in the AO basis set the experimental D_e of Ge_2 can be quantitatively reproduced. Moreover, the intershell correlation can also play an important role.

2.4.3.2 Electronic structure and charge distribution

The diagram of the energy levels for the $^3\Sigma_g^-$ ground state of Ge_2 is displayed in Fig. 2.4.6. From the analysis of this diagram it is evident that the π_u and $2\sigma_g$ MOs, which are mainly linear combinations of p orbitals, are of non bonding character with respect to the starting 4p AOs of the free Ge atoms. Moreover, the two bonding and antibonding combinations of 4s orbitals of σ_g and σ_u symmetry are separated by an energy gap of about 5.4 eV from the σ_p and π MOs. This energy separation is much smaller in C_2 than in both Si_2 and Ge_2 (244). This can be considered as a sign of a poor admixture of s and p AOs in the occupied MOs of Ge_2 .

The Mulliken population analysis of the natural orbitals for the ground state of Ge_2 supports this hypothesis (Table 2.4.7).

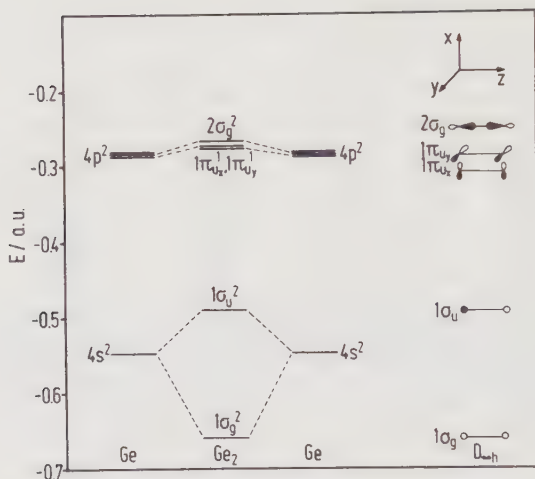


Fig. 2.4.6 - Schematic MO diagram for the interaction of two atoms to give the ${}^3\Sigma_g^-$ ground state of Ge_2 .

In fact, the electronic distribution of a Ge atom, $4s^2 4p^2$, remains almost unchanged in the dimer if the basis set I is employed. However, the introduction of d-functions in the AO basis set reinforces the electronic redistribution which occurs during the formation of the bond so that the final atomic population computed with the basis set III is practically $4s^{1.65} 4p^{2.35}$. The influence of d-functions is in particular clear from the population analysis of the σ MOs.

In fact the overlap of the d orbitals centered on the Ge atoms reinforces significantly the sp hybridization (Table 2.4.7). However, this effect involves only the p_σ orbitals, leaving practically unchanged the p orbitals of π symmetry.

Therefore, the data of population analysis show the preference of Ge_2 to assume a divalent electronic configuration more close to the $s^2 p^2$ atomic configuration rather than to the tetrahedral sp^3 hybrid atomic configuration which strongly stabilizes

Table 2.4.7 - Population analysis of the $^3\Sigma_g^-$ ground state of Ge_2 .

	$1\sigma_g$	$1\sigma_u$	$1\pi_u$	$2\sigma_g$	$1\pi_g^*$	Total
<i>Basis set I</i>						
4s	0.8788	0.9170	0.0000	0.1219	0.0000	1.9248
4p _z	0.1074	0.0597	0.0000	0.8471	0.0000	1.0445
4p _{x,y}	0.0000	0.0000	0.9721	0.0000	0.0511	1.0308
<i>Basis set II</i>						
4s	0.8249	0.8164	0.0000	0.1671	0.0000	1.8145
4p _z	0.1441	0.1446	0.0000	0.7907	0.0000	1.0986
4p _{x,y}	0.0000	0.0000	0.9464	0.0000	0.0395	0.9920
4d	0.0118	0.0084	0.0165	0.0067	0.0021	0.0949
<i>Basis set III</i>						
4s	0.8311	0.6453	0.0000	0.1624	0.0000	1.6464
4p _z	0.1367	0.2749	0.0000	0.7931	0.0000	1.2227
4p _{x,y}	0.0000	0.0000	0.9266	0.0000	0.0385	0.9714
4d	0.0128	0.0490	0.0263	0.0083	0.0022	0.1596

the diamond structure of Ge crystal.

This result can be considered as a further example of the analogies existing between Ge and Si dimers. Also in the case of Si_2 in fact the data of population analysis suggest that the Si atoms in the diatomic molecule assume a s^2p^2 electronic configuration (242).

2.4.3.3 Discussion of the properties of Ge_2

The numerous similarities found between Si_2 and Ge_2 potential energy curves cannot be fortuitous and can be attributed to the same kind of electronic structure characterizing these two dimers. This conclusion agrees with the findings of Harris and Jones (244) even if some qualitative discrepancies have been encountered in the determination of T_e for some excited states of Ge_2 (similar discrepancies have been found in the study of Si_2 with the AE MRD CI method (240,241)). On the other hand, very few analogies exist between the multiplet structure of Ge_2 and C_2 (248).

We summarize here some of the most important points which support these conclusions. The preferred electronic configuration

of Ge_2 is $\pi_{\text{u}}^2\sigma_{\text{g}}^2$, corresponding to the $^3\Sigma_{\text{g}}^-$ ground state. In contrast to the diatomic carbon, which is characterized by a $^1\Sigma_{\text{g}}^+$ ground state, the electronic configuration arising from the full occupation of the π_{u} MOs in the case of Si_2 and Ge_2 is less stable than the multiplet $\pi_{\text{u}}^2\sigma_{\text{g}}^2$.

The partial occupation of the upper $2\sigma_{\text{g}}$ MO, corresponding to the $\pi_{\text{u}}^3\sigma_{\text{g}}^1$ ($^3\Pi_{\text{u}}$) configuration, represents a compromise between the two limiting situations, namely $\pi_{\text{u}}^4\sigma_{\text{g}}^0$ and $\pi_{\text{u}}^2\sigma_{\text{g}}^2$. In fact the $^3\Pi_{\text{u}}$ is the first excited state, with a small energy separation from the ground state, in C_2 as well as in Si_2 and Ge_2 .

The differences existing in the ordering of the electronic states of the three dimers can be rationalized on the basis of the larger stability of the π -type MOs with respect to the σ ones in dimers of the first-row elements (240,241). Moreover, the tendency of Ge and Si to assume a divalent s^2p^2 electronic configuration contrasts with the preference typical of the carbon atom to undergo a strong sp hybridization in the molecular state.

The occurrence of strong hybridization is directly connected with the value of the atomic excitation energy for the transition $ns^2np^2 \rightarrow nsnp^3$. The smaller excitation energy for carbon ($33\,735\text{ cm}^{-1}$ (249)) than for Si and Ge ($48\,399$ and $55\,473\text{ cm}^{-1}$, respectively (249)) justifies the different amount of hybridization observed in C_2 , Si_2 and Ge_2 .

2.4.4 Small-size Ge_n clusters ($n = 3-7$)

2.4.4.1 Ge_3

Linear, "bent" and equilateral triangular are the three Ge trimers here considered (Table 2.4.8). In the bent form the Ge-Ge-Ge angle was fixed to the value 109.5 degrees, corresponding to the typical angle formed by sp^3 hybrid orbitals. Therefore this particular Ge_3 cluster can be considered as a section of the diamond-like Ge crystal lattice.

The results of Table 2.4.8 show that the stability of these

Table 2.4.8 - Electronic properties of Ge_3 clusters^{a)}

	spin multi- plicity ^{b)}	SCF			CI ^{c)}		
		r_e	E_T	D_e	r_e	E_T	D_e
Ge_3 "bent" (C_{2v})	s	4.47	-10.8132	14.7	4.52	-10.9722	68.8
	t	4.60	-10.7766	-8.2	4.78	-10.9245	38.9
	q	4.89	-10.7601	-18.6	4.91	-10.8999	23.4
Ge_3 linear ($\text{D}_{\infty h}$)	s	4.42	-10.8078	11.3	4.53	-10.9664	65.2
	t	4.90	-10.8134	14.9	4.94	-10.9469	52.9
	q	5.20	-10.8221	20.3	5.19	-10.9389	47.9
Ge_3 equilateral triangle (D_{3h})	s	5.08	-10.7190	-44.4	5.03	-10.8950	20.3
	t	5.00	-10.8014	7.3	5.09	-10.9560	58.6
	q	5.25	-10.7919	1.3	5.28	-10.9284	41.3

a) All values are in a.u. except the dissociation energies (D_e) which are in kcal/mole.

b) s = singlet, t = triplet, q = quintuplet.

c) Single reference CI.

clusters is mainly due to correlation effects and that in some cases clusters which are predicted to be unstable at SCF level are bound in the CI treatment.

On the contrary, the equilibrium bond lengths are not too sensitive to the inclusion of correlation effects and the computed interatomic distances are quite similar in SCF and CI. The Ge-Ge bond distances in bent and linear Ge_3 , 4.5 a.u., are slightly shorter than in Ge_2 (4.6 a.u.) (see Section 2.4.3.1). On the contrary, the interatomic distance in equilateral triangular Ge_3 is much larger (Table 2.4.8).

The sequence in stability of these three structures parallels that of the optimal distances. Bent and linear Ge_3 are the most stable trimers while the triangular form is clearly unfavorable.

Another significative difference between bent and linear Ge_3 on one side and the D_{3h} form on the other is that in the former clusters the ground state is a singlet while in the latter is a triplet.

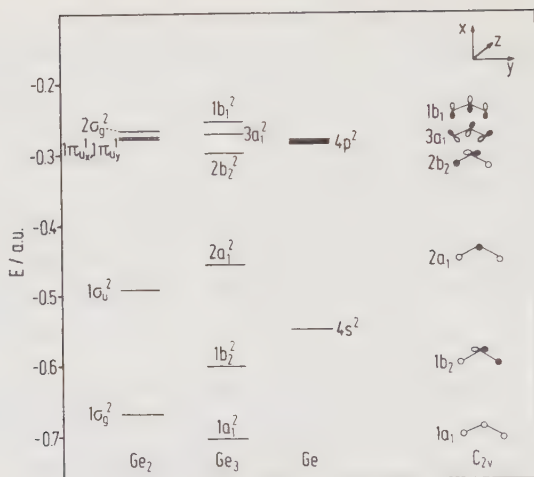


Fig. 2.4.7 - Energy and composition of the occupied MOs of bent Ge_3 (C_{2v}).

The Fig. 2.4.7 shows the MO diagram of bent Ge_3 as obtained by combining the MOs of Ge_2 with the AOs of a free Ge atom. The lowest $1a_1$, $1b_2$ and $2a_1$ MOs of Ge_3 are mainly composed from $4s$ orbitals while the contribution of $4p$ AOs is dominant in the $2b_2$, $3a_1$ and $1b_1$ MOs.

The deformation of the angle from 109 to 180 degrees (bent $\rightarrow$ linear) occurs with a very small destabilization of the cluster (about 3 kcal/mole) but without significant changes in the electronic structure.

The electronic configuration corresponding to the $^1\Sigma_g^+$ ground state of linear Ge_3 is $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(1\pi_u)^4(2\sigma_u)^2$ where the occupied MOs have the same character as in bent Ge_3 . Being the difference in stability between bent and linear Ge_3 clusters of the same order of magnitude as their vibrational energies it is not possible to conclude which is the most stable Ge trimer.

On the contrary, the deformation of bent Ge_3 to give the D_{3h} form is clearly an unfavoured process accompanied by a change in the electronic structure and spin multiplicity of the clu-

ster (Table 2.4.8). In fact, the $^1A_1'$ state of D_{3h} Ge_3 , with the configuration $(1a_1')^2(1e')^4(1a_2'')^2(2e'')^4$, is less stable than the $^3E'$ state corresponding to a simple HOMO-LUMO excitation of the singlet electronic configuration.

2.4.4.2 Ge_4

Six possible arrangements of Ge tetramers have been considered, namely rhombus, square, tetrahedron, T-form, "chain" and linear structures. The results for these clusters are summarized in Table 2.4.9.

The rhombic Ge_4 is the preferred form and the corresponding dissociation energy is appreciably larger not only with respect to that of other planar structures, such as square or T-shaped clusters, but also in comparison with the D_e of the more compact tetrahedral arrangement. As for alkali metal clusters (Chapter 2.1), also for Ge tetramers the criterion of the

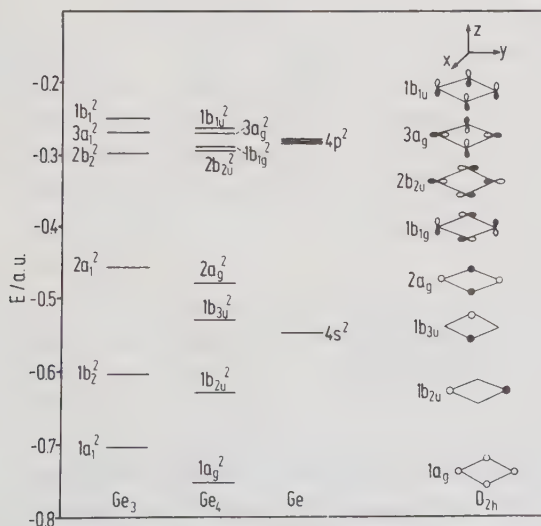


Fig. 2.4.8 - Energy and composition of the occupied MOs of rhombic Ge_4 (D_{2h}).

Table 2.4.9 - Electronic properties of Ge₄ clusters^{a)}

	spin multi- plicity ^{b)}	SCF			CI ^{c)}		
		r _e	E _T	D _e	r _e	E _T	D _e
Ge ₄ rhombus (D _{2h})	s	4.94	-14.4771	56.9	5.02	-14.6474	121.1
	t	5.05	-14.4380	33.4	5.05	-14.6384	97.3
	q	5.38	-14.3947	5.3	5.43	-14.5753	57.6
Ge ₄ square (D _{4h})	s	5.01	-14.4235	23.3	5.03	-14.6213	86.5
	t	4.92	-14.4354	30.8	4.99	-14.6344	94.7
	q	5.14	-14.4318	28.6	5.17	-14.6037	75.5
Ge ₄ T-form (C _{2v})	s	4.93	-14.4284	26.4	4.98	-14.6302	92.1
	t	4.92	-14.4462	37.6	4.97	-14.6268	90.0
	q	5.04	-14.4321	28.7	5.09	-14.6040	75.7
Ge ₄ tetrahedron (T _d)	s	5.37	-14.4021	9.9	5.43	-14.6107	79.8
	t	5.41	-14.3588	-17.3	5.45	-14.5697	54.1
	q	5.40	-14.3954	5.7	5.44	-14.5821	61.9
Ge ₄ "chain" (C _{2h})	s	4.67	-14.3914	3.1	4.65	-14.5854	64.0
	t	4.98	-14.4127	16.5	4.94	-14.5773	58.9
	q	4.91	-14.4156	18.3	4.90	-14.5806	61.0
Ge ₄ linear (D _{∞h})	s	5.17	-14.2796	-66.9	5.17	-14.4899	4.1
	t	5.21	-14.3081	-49.0	5.25	-14.5075	15.1
	q	5.25	-14.3570	-18.4	5.27	-14.5199	22.9

a) All values are in a.u. except the dissociation energies (D_e) which are in kcal/mole.

b) s = singlet, t = triplet, q = quintuplet.

c) Single reference CI.

"maximum number of bonds" is violated.

Even less stable than the tetrahedron are the open structures like linear or chain Ge₄. This latter is an extension of the bent Ge₃ and represents a segment of the Ge crystal lattice.

The valence MOs of rhombic Ge₄ (Fig. 2.4.8) are divided into two groups, a first set of MOs (1a_g, 1b_{2u}, 1b_{3u}, and 2a_g) which are nearly pure combinations of 4s atomic orbitals and a second set of MOs (2b_{2u}, 1b_{1g}, 3a_g and 1b_{1u}) mainly composed from 4p atomic orbitals. These two sets of MOs are separated by an energy gap of 5 eV which is ten times larger than the same

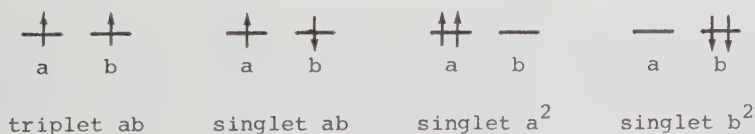
quantity computed with the AE MRD CI method for the isovalent rhombic C_4 cluster (250). The large separation between MOs with prevailing s and p character is a sign of the weaker sp hybridization occurring in Ge clusters with respect to analogous carbon clusters.

The ground state of rhombic Ge_4 , 1A_g , is separated by about 25 kcal/mole from the lowest triplet state, $^3B_{3g}$. The respective potential energy curves computed with and without d-polarization functions are shown in Fig. 2.4.2. An equilibrium bond length 5.0 a.u. for both singlet and triplet states is obtained with the basis set without d-functions. This bond length is shortened by about 0.2-0.3 a.u. when d-functions are considered (Fig. 2.4.2).

The optimization of the angle of the rhombus (performed with the basis set without d-functions) gives the optimum value 115 degrees for the singlet ground state. The further deformation of this angle to give the square arrangement is accompanied by a drastic change in the electronic structure of the cluster resulting in a different ground state (triplet) (Fig. 2.4.9).

On going from the rhombus (D_{2h}) to the square (D_{4h}) Ge_4 the occupied $2b_{2u}$ and the virtual $2b_{3u}$ MOs of the rhomb transform into the degenerate $2e_u$ MOs in D_{4h} which are the partly occupied HOMOs of the cluster.

Four electronic configurations of square Ge_4 are possible, according to the scheme:



The triplet ab is the ground state of the cluster and is separated by only 7 kcal/mole from the singlet ab. The linear combination of the two singlet electronic configurations a^2 and b^2 (a^2+b^2 , a^2-b^2) gives rise in CI to two singlet states displaying a typical biradical character.

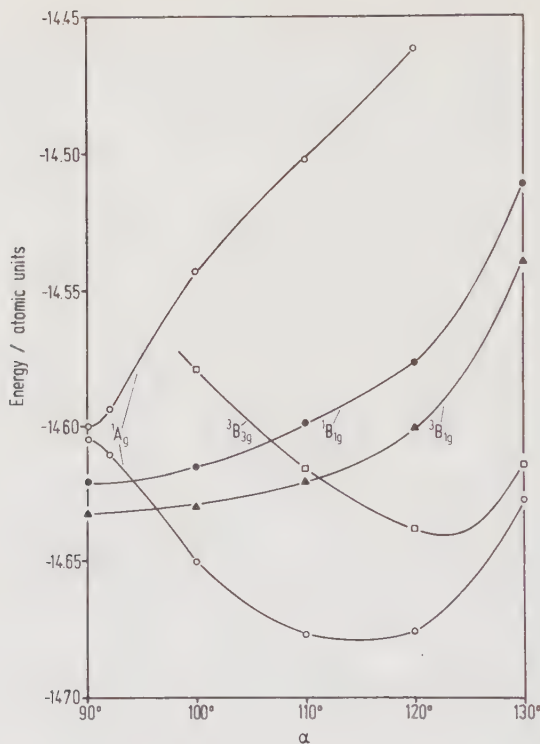


Fig. 2.4.9 - Potential energy curves for the process $\text{Ge}_4 (\text{D}_{4h}) \rightarrow \text{Ge}_4 (\text{D}_{2h})$. The Ge-Ge bond distance has been fixed to the value 5.0 a.u. .

Both these latter states are slightly higher in energy than the singlet and the triplet ab (Fig. 2.4.9). However, with the deformation of the geometry from D_{4h} to D_{2h} the singlet a^2+b^2 ($^1A_{1g}$ in D_{4h}) is strongly stabilized and gives the 1A_g ground state of rhombic Ge_4 . The larger stability of the rhombus with respect to the square is characteristic not only for Ge tetramers but also for C and alkali metal clusters (250).

Among the other Ge_4 clusters considered, the tetrahedral form in its equilibrium geometry has a singlet ground state

corresponding to the valence electronic configuration $(1a_1)^2 (1t_2)^6 (2a_1)^2 (2t_2)^6$. This high symmetrical form of Ge_4 is about 40 kcal/mole less stable than the rhombus.

The last two Ge tetramers considered are the linear and the chain forms. It is worth noting that this latter geometry is similar to the arrangement of Ge atoms found in the inorganic complex $\text{Ge}_4 \text{Ph}_4 \text{I}_2$ (251) by means of X-ray diffraction measurements. However, nor the linear neither the chain forms are stable Ge tetramers. Linear Ge_4 has a quintuplet ground state. The potential energy curve for the process $2\text{Ge}_2 \rightarrow \text{linear Ge}_4$ is purely repulsive.

The loss of linearity of this cluster to give the chain one is accompanied by an appreciable gain in stability (Table 2.4.9) and by a change in spin multiplicity of the ground state which is a singlet separated by a small energy gap from the lowest quintuplet (Table 2.4.9).

The result that linear Ge_4 is an unfavoured structure contrasts with the remarkable stability of the corresponding linear C_4 cluster (252). The difference in stability of the two clusters can be rationalized on the basis of the different amount of sp hybridization in C and Ge. The large stability of the π -type MOs in C clusters facilitates the formation of multiple bonds which on the contrary are quite unfavoured in corresponding Ge clusters. On the other hand, it is just the formation of π bonds which makes the linear form of C_4 comparable in stability with the rhombic one (250).

The different tendency to form sp hybrids is a characteristic feature also of C_2 and Ge_2 molecules where this effect is responsible for the different electronic structure and ground states observed (see Section 2.4.3.3).

2.4.4.3 Ge_5

Previously performed investigations on alkali metal clusters have shown that planar clusters can be as stable as more compact arrangements and in some cases even more stable. Similarly, large planar Be clusters compete in stability with tridimensional structures.

Table 2.4.10 - Electronic properties of Ge_5 clusters^{a)}

	spin multi- plicity ^{b)}	SCF			CI ^{c)}		
		r_e	E_T	D_e	r_e	E_T	D_e
Ge_5 trigonal bipyramid (D_{3h})	s	5.31	-18.0571	46.5	5.36	-18.2990	122.2
	t	5.32	-18.0821	62.2	5.32	-18.3167	133.3
	q	5.55	-18.0363	33.5	5.63	-18.2443	87.8
Ge_5 trapezium (C_{2v})	s	4.97	-18.0591	47.8	5.01	-18.3039	125.3
	t	5.04	-18.0756	58.1	5.05	-18.3081	127.9
	q	5.25	-18.0359	33.3	-	-	-
Ge_5 square pyramidal (C_{4v})	s	5.23	-18.0444	38.6	5.25	-18.2985	121.8
	t	5.25	-18.0328	31.3	5.21	-18.2667	101.9
	q	5.32	-18.0696	54.4	5.37	-18.2812	111.0
Ge_5 tetrahedron (T_d)	s	4.85	-17.9188	-40.2	4.81	-18.1623	36.4
	t	4.99	-17.9975	9.1	4.93	-18.2102	66.4
	q	4.97	-18.0548	45.6	4.98	-18.2582	96.5
Ge_5 linear ($D_{\infty h}$)	s	5.02	-17.9264	-35.4	5.03	-18.1611	35.6
	t	4.67	-17.9540	-18.1	4.69	-18.1963	57.7
	q	4.58	-17.9910	5.1	4.63	-18.2013	60.9

a) All values are in a.u. except the dissociation energies (D_e) which are in kcal/mole.

b) s = singlet, t = triplet, q = quintuplet.

c) Single reference CI.

The relative instability of tetrahedral Ge_4 and C_4 in comparison with the corresponding rhombic tetramers confirms this tendency also for the Group IVA clusters. Therefore, the investigation of Ge pentamers has been performed for both planar and non-planar structures. In particular five geometries have been considered, namely the trigonal bipyramid, the square pyramid, the centered tetrahedron, the linear and a planar trapezium of C_{2v} symmetry obtained by joining three equilateral triangles.

This latter structure represents a planar extension of the very stable rhombic Ge_4 and is very stable as well. Its total energy is similar to that of the more close-packed bipyramidal trigonal and square pyramidal Ge pentamers (Table 2.4.10).

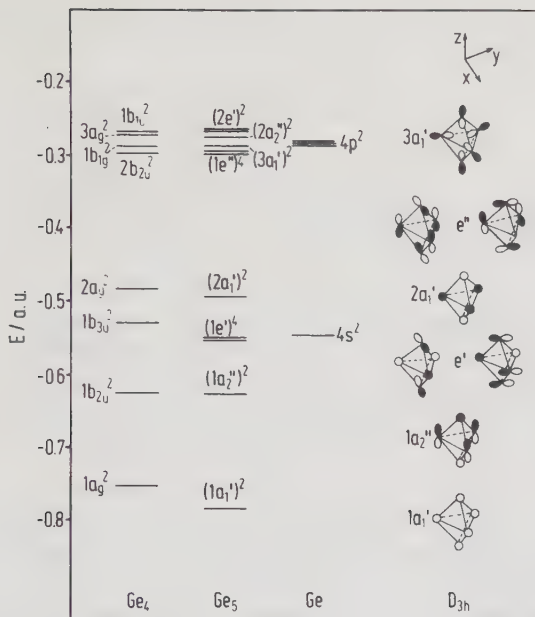


Fig. 2.4.10 - Energy and composition of the occupied MOs of trigonal bipyramid Ge_5 (D_{3h}).

The single reference CI treatment gives comparable stabilities for the three clusters (Table 2.4.10).

The triplet ground state of bipyramidal trigonal Ge_5 is due to the existence of the degenerate HOMOs of e' symmetry which are not fully occupied (Fig. 2.4.10). In square pyramidal Ge_5 the HOMO of a_1 symmetry is doubly occupied and the ground state is therefore a singlet. In planar $\text{Ge}_5(\text{C}_{2v})$, the singlet and the triplet electronic configurations $(\dots)(a_2)^2$ and $(\dots)(a_2)^1(b_2)^1$ are separated by about 10 kcal/mole in SCF (triplet lower than singlet) while the single main CI gives the two states nearly degenerate (Table 2.4.10).

Finally, the multireference CI treatment (3M) predicts for $\text{Ge}_5(\text{C}_{2v})$ a singlet ground state with the triplet lying only 4 kcal/mole higher than the singlet.

This is a sign of the existence of close-lying states even for small-size germanium clusters.

The very small stability of linear Ge_5 is not unexpected because of the previously discussed weak ability of Ge clusters to form π bonds. On the contrary, the relatively small D_e of the tetrahedric form of Ge_5 is rather surprising if we consider that this cluster is a segment of the Ge crystal lattice. In this structure in fact the central atom has the same coordination as a bulk Ge atom. Despite the possibility for this central atom to strongly interact through the formation of sp^3 hybrid orbitals with the peripheral atoms placed at the vertices of a regular tetrahedron, we found that the $\text{Ge}_5(T_d)$ cluster is 25-35 kcal/mole less stable than the D_{3h} , C_{2v} and C_{4v} structures (Table 2.4.10).

The reason for the relative instability of the tetrahedric form of Ge_5 is to be looked for in the too large distance separating the peripheral atoms (about 8 a.u.). Therefore, while in bipyramidal trigonal Ge_5 every atom is interacting with 4 nearest neighbors, in tetrahedral Ge_5 only the central Ge atom has this number of nearest neighbors, the remaining atoms interact only with the central one. The unsaturation of the valence of the four peripheral atoms and the small compactness of the cluster are the reasons for the relatively small stability of this structure.

2.4.4.4 Ge_6 -

Among the Ge hexamers considered the three closed-packed structures monocapped trigonal bipyramid (C_{2v}), octahedron (O_h) and pentagonal pyramid (C_{5v}) are much more stable than the hexagonal planar (D_{6h}) and "chair" hexagonal (D_{3d}) forms (this latter cluster is a section of the Ge crystal being the Ge-Ge-Ge angles fixed to the value 109.5 degrees).

The monocapped trigonal bipyramid and the octahedron show very similar dissociation energies. The single main CI treatment gives the C_{2v} cluster 3 kcal/mole more stable than the O_h one, and according to the multireference CI (3M) the stabilities of

Table 2.4.11 - Electronic properties of Ge_6 clusters^{a)}

	spin multi- plicity ^{b)}	SCF			c) CI		
		r_e	E_T	D_e	r_e	E_T	D_e
Ge_6 monocap. trig. pyramid (C_{2v})	s	5.25	-21.6593	72.6	5.30	-21.9496	170.4
	t	5.41	-21.6612	51.4	5.42	-21.9132	147.6
	q	5.52	-21.6383	37.0	5.52	-21.8706	120.9
Ge_6 octahedron (O_h)	s	5.41	-21.6665	54.6	5.48	-21.9092	145.1
	t	5.31	-21.6988	74.8	5.37	-21.9439	166.9
	q	5.37	-21.6336	33.9	5.46	-21.8699	120.5
Ge_6 pentagonal pyramid (C_{5v})	s	5.26	-21.6573	48.8	5.27	-21.9025	140.9
	t	5.29	-21.6785	62.1	5.28	-21.9187	151.1
	q	5.26	-21.6752	60.0	5.25	-21.9076	144.1
Ge_6 "chair" hexagonal (D_{3d})	s	5.05	-21.6442	40.6	4.96	-21.8516	109.0
	t	4.90	-21.6439	40.5	4.91	-21.8660	118.0
	q	4.97	-21.6231	27.4	4.96	-21.8417	102.8
Ge_6 hexagonal (D_{6h})	s	5.02	-21.5347	-16.3	5.06	-21.7815	65.0
	t	5.17	-21.5570	-14.1	5.23	-21.7722	59.1
	q	5.01	-21.5783	- 0.7	5.03	-21.7880	69.1

a) All values are in a.u. except the dissociation energies (D_e) which are in kcal/mole.

b) s = singlet, t = triplet, q = quintuplet.

c) Single reference CI.

the two clusters differ by 8 kcal/mole. These two structures are obtained by growing the trigonal bipyramid and the square pyramidal Ge_5 clusters which also show similar stabilities. However, while the ground state of the trigonal bipyramid Ge_5 is a triplet, in the monocapped form of Ge_6 of C_{2v} symmetry the degeneracies present in the $\text{Ge}_5(D_{3h})$ cluster are removed and the ground state is a singlet (in Fig. 2.4.11 is shown the character of the occupied MOs).

On the contrary, the addition of one atom to the base of the square pyramid (singlet ground state) yields the octahedric form and is accompanied by the appearance of not fully occupied degenerate HOMOs. Therefore, the ground state of the O_h cluster is a triplet (Table 2.4.11).

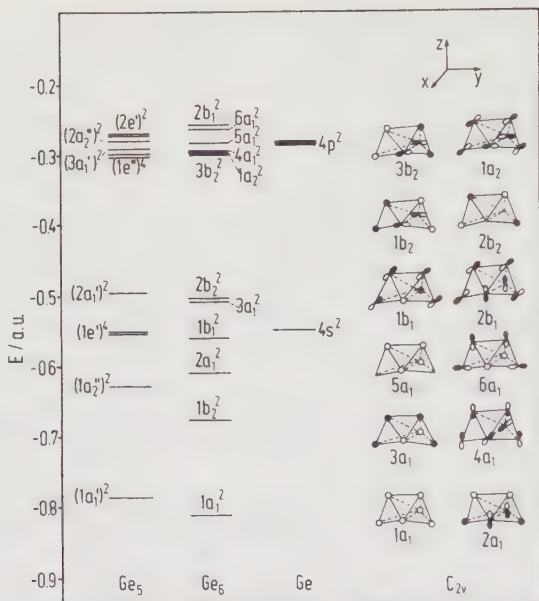


Fig. 2.4.11 - Energy and composition of the occupied MOs of monocapped trigonal bipyramidal Ge_6 (C_{2v}).

The pentagonal pyramidal Ge_6 has been investigated because the analogous Li_6 cluster was found very stable. Our calculations confirm that this structure with pentagonal symmetry is favourable, although the D_e of the $\text{Ge}_6(\text{C}_{5v})$ cluster is slightly smaller than that of the previously discussed C_{2v} and O_h Ge hexamers (Table 2.4.11).

Very unfavourable are the two hexagonal structures considered, the "chair" and the planar one. In both these structures every Ge atom interacts with only two nearest neighbors. An activation barrier of 50 kcal/mole separates the more stable chair form from the planar one which can be considered as the activated complex in the twisting reaction of the chair conformation.

The Ge_6 cluster with the hexagonal chair conformation has been experimentally observed in the molecular clusters $(\text{GeMe}_2)_6$

Table 2.4.12 - Electronic properties of the Ge_7 cluster^{a)}

	spin multi- plicity ^{b)}	SCF			CI ^{c)}		
		r_e	E_T	D_e	r_e	E_T	D_e
Ge_7 pentagonal bipyramid (D_{5h})	s	5.34	-25.3787	126.6	5.36	-25.6554	228.7
	t	5.42	-25.3115	85.0	5.41	-25.5856	184.9

a) All values are in a.u. except the dissociation energies (D_e) which are in kcal/mole.

b) s = singlet, t = triplet.

c) Single reference CI.

(253) and $(\text{GePh}_2)_6 \cdot 7 \text{C}_6\text{H}_6$ (254). In these compounds the Ge atoms are in a tetrahedric coordinative position and their sp^3 valence is completely saturated through the bonding with the methyl and phosphine groups. The role of the organic ligands is just that to stabilize a cluster-unit having small intrinsic stability.

2.4.4.5 Ge_7

The existence of metal clusters with five-fold symmetry axis has been experimentally (70) and theoretically (76) demonstrated for the case of alkali metals.

Moreover, structures with icosahedral or pentagonal symmetry have been proposed in order to interpret the observed "magic numbers" in the mass spectra of clusters of various elements.

Therefore, we have studied the pentagonal bipyramid form of Ge_7 with the particular aim to compare its stability with that of smaller Ge aggregates.

The singlet state of $\text{Ge}_7(D_{5h})$ is very stable with respect to the dissociation into Ge atoms. The binding energy per atom computed with the single reference CI treatment, 32.7 kcal/mole, (Table 2.4.12) is the largest one among all the structures here considered. The valence singlet electronic configuration is $(1a_1')^2 (1e')^4 (1a_2'')^2 (2e')^4 (2a_1')^2 (1e'')^4 (3a_1')^2 (3e')^4 (4e')^4$ where, once more, the seven lowest MOs have s-character while the remaining seven

MOs are mainly combinations of p-orbitals. The triplet state has been obtained by excitation of one electron from the $4e'$ HOMO to the $2a_2''$ LUMO of the cluster, but the corresponding energy is considerably higher than that of the singlet ground state.

2.4.5 Discussion of the stability and structure of Ge clusters

The total energy of the Ge clusters here considered has been determined for the optimal geometries with multireference CI calculations. Three or more leading configurations have been chosen to generate the CI space. The contribution of higher excitations than single and double to the total CI energy (full CI) has been evaluated by means of the Davidson formula (see Section 1.2.3).

The full CI binding energies of Ge clusters are compared with the corresponding experimental values (Table 2.4.13). At first glance, the discrepancy between computed and measured dissociation energies is quite large, the theoretical values representing only 50-60 per cent of the experimental ones.

Many factors can contribute to this result. First, the basis set used is rather poor and the inclusion of d, and eventually of f, functions could be important for the evaluation of D_e . Some effects which are not taken into account in our calculations can also influence the stability of the cluster.

For example, the inclusion of 3d electrons in the atomic core can reduce the bonding ability of Ge atoms. Moreover, the neglect of core-polarization, inter-shell correlation and relativistic effects is surely causing an underestimation of D_e .

Finally, a further error in the determination of D_e is introduced by the definition in our calculations of D_e as

$$D_e = \left\{ E_{\text{full CI}}(\text{Ge}_n) - n \left[E_{\text{full CI}}(\text{Ge}) \right] \right\}.$$

Because of the appearance of size effects in the CI treatment with increasing cluster size, the CI wave function and the CI energy of a single Ge atom are better described than the corresponding quantities of a Ge cluster. This error is quite small

Table 2.4.13 - Estimated full CI energies and stabilities of Ge clusters

	spin multi- plicity of the ground state	a) theoretical treatment nM/ $\sum_i c_i^2$	c) $E_{\text{full CI}}$ (a.u.)	D _e (Kcal/mole)	
				theor.	exp. ^{d)}
Ge ₂ (D _{∞h})	t	3M/ .92	- 7.3047	39.4	61± 2
Ge ₃ (C _{2v})	s	3M/ .86	-11.0051	88.2	155± 4
Ge ₃ (D _{3h})	s	3M/ .85	-11.0024	86.5	
Ge ₃ (D _{3h})	t	3M/ .87	-10.9821	73.8	
Ge ₄ (D _{2h})	s	3M/ .85	-14.7160	144.3	243± 8
Ge ₄ (D _{4h})	t	3M/ .85	-14.6755	118.9	
Ge ₄ (C _{2v})	s	3M/ .85	-14.6710	116.0	
Ge ₄ (T _{2d})	s	3M/ .84	-14.6619	110.4	
Ge ₄ (C _{2h})	s	4M/ .84	-14.6252	87.3	
Ge ₄ (D _{∞h})	q	3M/ .87	-14.5455	37.3	
Ge ₅ (D _{3h})	t	3M/ .85	-18.3619	159.6	322± 10
Ge ₅ (C _{4v})	s	3M/ .85	-18.3637	160.8	
Ge ₅ (C _{2v})	s	3M/ .84	-18.3562	156.0	
Ge ₅ (T _{2d})	q	3M/ .90	-18.2774	106.6	
Ge ₅ (D _{∞h})	q	3M/ .84	-18.2290	76.2	
Ge ₆ (C _{2v})	s	3M/ .83	-22.0061	204.5	412± 13
Ge ₆ (O _h)	t	3M/ .83	-21.9926	196.1	
Ge ₆ (C _{5v})	t	3M/ .84	-21.9610	176.2	
Ge ₆ (D _{3d})	t	3M/ .83	-21.9152	147.5	
Ge ₆ (D _{6h})	q	3M/ .83	-21.8210	88.5	
Ge ₇ (D _{5h})	s	3M/ .82	-25.7043	257.8	490± 16

a) s = singlet, t = triplet, q = quintuplet.

b) nM indicates the number of reference configurations from which all single and double excitations are generated. All configurations which contribute more than 0.5 per cent to the CI expansion are chosen as leading configurations. $\sum_i c_i^2$ gives the total weight of the main configurations in the final CI wave function.

c) Full CI energy estimated according to the Davidson formula (120).

d) From ref. (15).

for the dimer, but increases with the number of atoms in the cluster.

Despite these facts which are responsible for the differences observed, the theoretical description of the stability of small Ge clusters versus the cluster size qualitatively agrees with the experimental data (Fig. 2.4.12). The shape of the two

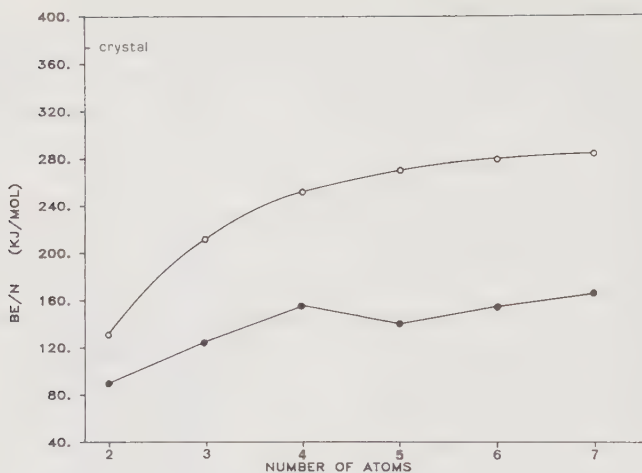


Fig. 2.4.12 - Experimental (o) (15) and theoretical (●) binding energies per atom (BE/n) for Ge clusters.

curves, experimental and theoretical, is similar and indicates a rapid increase of the cluster stability for the small terms of the series (Ge_2 - Ge_4) while for larger Ge clusters the binding energy per atom grows rather slowly with the increasing cluster size (Fig. 2.4.12).

Ge clusters are stable not only with respect to the dissociation into separated atoms but also in comparison to smaller fragments. For example, rhombic Ge_4 is 64 kcal/mole more stable than two Ge_2 molecules. When the basis set without d-functions is considered, also square and T-shaped Ge_4 clusters are about 30-35 kcal/mole more favoured than two Ge dimers, but when d-functions are considered only the rhombus is still favoured with respect to the fragmentation into dimers, while the energy of the square Ge_4 equals the sum of the energies of two diatomic molecules.

This is due to the larger stabilization produced by the d-functions in Ge_2 than in square Ge_4 (compare Fig. 2.4.3 and 2.4.4 and Section 2.4.3.1).

The dissociation of Ge_5 into Ge_2 and Ge_3 is also an unfavorable process. The trigonal bipyramid Ge_5 is in fact 32 kcal/mole more stable than two non-interacting Ge_2 and Ge_3 moieties (Table 2.4.13).

Finally, the dissociation processes $\text{Ge}_6 \rightarrow 2 \text{Ge}_3$ and $\text{Ge}_7 \rightarrow \text{Ge}_3 + \text{Ge}_4$ need 28 and 25 kcal/mole, respectively, in order to occur (Table 2.4.13). Therefore, the ΔE for these fragmentation processes are decreasing with the increasing cluster size, in agreement with the experimental data (the measured ΔE for the processes $\text{Ge}_4 \rightarrow 2 \text{Ge}_2$, $\text{Ge}_5 \rightarrow \text{Ge}_2 + \text{Ge}_3$, $\text{Ge}_6 \rightarrow 2 \text{Ge}_3$ and $\text{Ge}_7 \rightarrow \text{Ge}_3 + \text{Ge}_4$ are 113, 105, 101 and 89 kcal/mole, respectively). This suggests that slightly larger clusters could be unfavoured with respect to the fragmentation into smaller highly stable clusters (e.g. rhombus Ge_4).

A possible mechanism of the cluster growth can be deduced from the data of Table 2.4.13. The process $\text{Ge}_2 + \text{Ge}$ leads to the formation of the bent Ge_3 in equilibrium with the linear form. For this cluster the compactness of the structure is not the most important factor. Similar arguments are valid for Ge tetramers, being the planar rhombus much more stable than the compact tetrahedron.

Among Ge_5 clusters considered, the closed-packed structures trigonal bipyramid and square pyramid, where the average number of nearest neighbors is 3.6 and 3.2, respectively, are only slightly more stable than the planar trapezoid Ge_5 (average number of nearest neighbors 2.8). For larger clusters the criterion of maximum number of bonds seems to become more important as demonstrated by the fact that the most stable Ge_6 (monocapped trigonal bipyramid and octahedron) and Ge_7 (pentagonal bipyramid) clusters have an average number of nearest neighbors equal to 4, 4 and 4.3, respectively.

None of these structures represent either a regular or a deformed section of the germanium crystal lattice. On the contrary, most stable Ge clusters can be considered segments of closed-packed crystal lattices or steps in a pentagonal crystal growth.

Germanium crystal is strongly stabilized by a tridimensional

Table 2.4.14 - Average population of most stable Ge clusters

system	4s population	4p population
free Ge atom	2.00	2.00
Ge ₂ (D _{∞h})	1.90	2.10
Ge ₃ (C _{2v})	1.79	2.21
Ge ₄ (D _{2h})	1.88	2.12
Ge ₅ (D _{3h})	1.96	2.04
Ge ₅ (T _d) a)	1.72	2.28
Ge ₆ (C _{2v})	1.89	2.11
Ge ₇ (D _{5h})	1.91	2.09
sp ³ bulk crystal	1.00	3.00

a) Central Ge atom.

network of sp³ hybrid orbitals centered on every Ge atom. The valence of Ge atoms in crystal is saturated by the bonding with four nearest neighbors located at the apices of a regular tetrahedron. In order to have such kind of bonding a very large number of atoms is necessary to minimize the "edge" effects due to the unsaturation of the surface atoms.

Of course, the electronic structure of a small cluster containing few germanium atoms cannot resemble that of an infinite network of sp³ hybrid orbitals. The average atomic population in a small Ge cluster is different from that of the Ge crystal.

The 4s orbital population, varying between 1.8 and 1.95 electrons (Table 2.4.14), indicates that the Ge atoms in a cluster have an electronic configuration very close to that of a free Ge atom. The electronic redistribution occurring on Ge atoms as a consequence of the formation of the Ge-Ge bonds in the cluster is therefore rather small. In tetrahedral Ge₅ the central Ge atom, which has the same coordination as a bulk atom, shows an electron population markedly different from that of a sp³ hybrid (Table 2.4.14).

The clear tendency of small Ge clusters to assume geome-

trical and electronic structures completely different from that of the bulk crystal can be connected with the experimental evidence of the reconstruction of the (111) Ge surface.

Photoemission measurements (255) give direct experimental evidence of occupied surface states on the (2x1) reconstructed surface. This reconstruction causes the dangling bonds of the surface atoms to partially rehybridize from bulk sp^3 into more s-like (sp^2+p) orbitals (255). The final surface arrangement differs substantially from the ideal truncated lattice resulting in a buckled compact structure.

Recent pseudopotential local density calculations for Ge (111)-(2x1) using the Hellmann-Feynman Forces to determine stable structures have shown that this kind of rehybridization is energetically favourable and that it occurs naturally as the position of the surface atoms is changed (256).

2.5 GENERAL CONCLUSIONS[#]

2.5.1 Quantum chemistry in the research on clusters

The dramatic development in the experimental surface science and in the isolation techniques of small atom aggregates as well as a rapid improvement of the ab initio quantum chemical methods (and a much easier accessibility to the computers) have caused recently a spectacular increase of the theoretical investigations of the clusters with the quantum chemical approaches of various degree of sophistication.

The impact of this kind of theoretical investigation for the understanding of electronic structures of clusters and the theory of crystal growth is evident. It is unclear if and how cluster studies can contribute to the fundamental problems of the theory of surface properties of metals and semiconductors. In particular, one can ask if necessarily small or medium size clusters can model the chemisorption behaviour and catalytic properties of solid surfaces. The mystery if the catalytic activity of solids is due to local chemical characteristics or to the global peculiarities of the crystals is of very old date but still represents an unsolved problem.

The simple enlargement of clusters leading to a situation in which the reasonable fraction of atoms involved has the same number of nearest neighbors as in the model system is not feasible if the quality of the quantum chemical method employed should remain on the acceptable level of sophistication.

The level of sophistication is given by the extent and properties of the basis set used for the expansion of the one-electron functions for the investigated system and by the manner in which electron correlation effects are taken into account. The flexibility of the AO basis set can be of a basic importance for the qualitatively proper description of the electronic structure of clusters mainly if the bonding in the cluster is rather weak.

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The present chapter has been partly published in the paper /5/ of the list of p. 201 .

Therefore it is not surprising that the description of mainly small metal clusters is critically sensitive to the AO basis set used.

A very promising and recently widely employed way how to bypass the bottle-neck of too large size of the AO basis set is the use of pseudopotential approaches. It is perhaps appropriate to emphasize that seemingly technical details of the quantum chemical procedures are closely related to the physical and chemical nature of investigated cluster systems. The properly interpreted properties of an appropriate AO basis set shows clearly some basic features of the bonds between the atoms involved in the studied system. It is more the character of the AO basis functions than the extent of the basis set which determines if the chemical bond is basically well described. A relatively small AO basis set can be very helpful for qualitative understanding of chemical bonds involved. A further extension of the AO basis set can then influence only quantitatively the results. This "AO basis set saturation" is reached naturally easier for larger systems where the AOs centered on neighboring atoms help to give the necessary larger flexibility to the overall basis set.

The analysis of the one-electron functions (molecular or natural orbitals) based necessarily also on the understanding of the meaning of the AO basis functions is a comfortable tool for a qualitative explanation of the cluster stability.

The quality of approaches employed for investigation of various clusters allows to draw some interesting conclusions of quite a general character. For this reason, in this chapter the question will be discussed to which extent chemical properties of large systems which are interesting for practical purposes can be extrapolated from the knowledge of the electronic structure of relatively small clusters.

The properties of alkali metal, alkaline-earth metal and aluminium clusters will be analyzed from the above mentioned point of view and compared with clusters of "non-metallic" atoms like germanium.

2.5.2 Geometry and electronic structure of small clusters

2.5.2.1 Group Ia clusters

In Li aggregates and in general in all alkali metal clusters, the bonds originate from the interaction of the outer s orbitals. However, the overlap between s orbitals is strongly stabilized by the consideration of the p-polarization functions.

The bond in lithium clusters is in general delocalized over many atomic centers. The concept of multi-center-bond is essential for the proper understanding of the electronic structure of these clusters. A typical example of such a bond is given by the rhombic Li_4 cluster. The corresponding differential electron density map (Fig. 2.5.1), computed as the difference between the electron density of the cluster and that of the separated atoms, clearly shows the existence of a three-center bond which disappears in the less favoured square Li_4 cluster (Fig. 2.5.2).

The similarity in the nature of the bond in Li clusters and Li crystal explains, on the basis of the cluster results, some properties found with the metal. For example, the average bond strength, expressed in terms of binding energy per atom (BE/n), does not change strongly along some deformation path, as long as no new overlap between covalent atomic radii takes place. The "bond topology" (it means the number of nearest neighbors for individual cluster atoms) is a more important factor than the small changes in bond distances for the cluster stability. This property is due to the role of p-orbitals as polarization functions and explains the softness of lithium and of alkali metals in general.

However, the usual concept of maximum number of bonds does not apply in a simple way to this class of clusters. Planar Li_4 is in fact much more stable than the very compact tetrahedron, a result recently confirmed by experiments (18).

Among larger Li clusters, planar structures are in competition with clusters which can be considered as steps in the pentagonal crystal growth (e.g. pentagonal bipyramid Li_7) (70).

Two general effects concur to the determination of the most stable geometry: the Jahn-Teller effect and the tendency towards

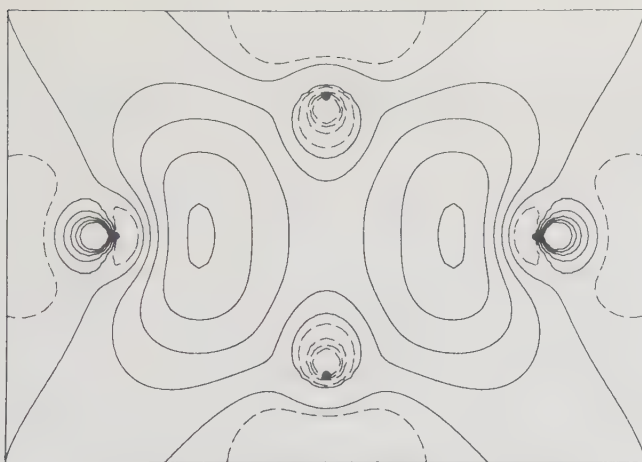


Fig. 2.5.1 - Differential electron density map for rhombic Li_4 . The map is computed as the difference between the electron density of the cluster and that of the spherical atoms placed at equilibrium distance. The dotted lines indicate a lowering, the full lines an increase of the electron density.

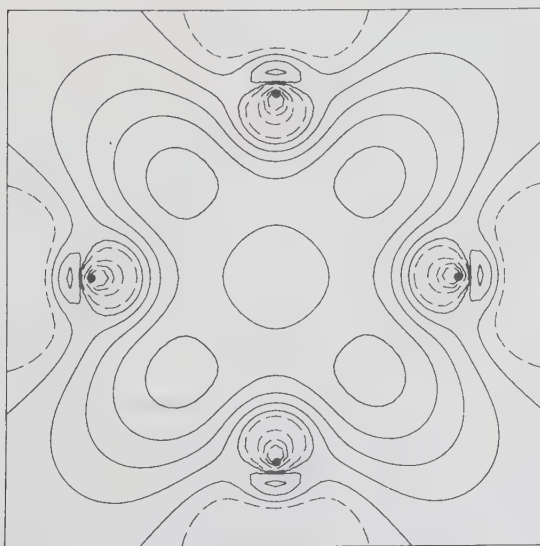


Fig. 2.5.2 - Differential electron density map for square Li_4 (see Fig. 2.5.1 for definitions).

the most compact arrangement. Only the appropriate analysis of the electronic structure of the cluster can lead to the correct prediction of the preferred geometry of the cluster.

Similar conclusions are valid also for clusters of heavier alkali metal atoms in virtue of the similarities found in the electronic structures of Li, Na and K clusters. It has been also found that the rhombic form is the most stable geometry for the singlet state of Na_4 clusters, while the square arrangement is preferable for the triplet state. It has been confirmed that for K tetramers the singlet rhombus K_4 is more favoured than the triplet square K_4 , but the energy difference between the two forms decreases in the series Li, Na, K. Moreover, with the increase of the atomic number the difference in stability between rhombic and other tetraatomic structures becomes smaller.

2.5.2.2 Group IIa clusters

The interaction of two Be atoms (characterized by an He-like atomic configuration) is expected to be an unfavoured process, as confirmed by the absence of experimental evidence for the existence of a stable Be_2 molecule (209,214).

The combination of three Be atoms in a linear or triangular geometry indicates that these structures are very weakly bonded species and the inclusion of d-functions in the AO basis set is necessary in order to obtain a small dissociation energy. Similarly, also square or rhombic Be tetramers are very weakly bonded species. Their binding energy is in fact a few kcal/mole and the equilibrium bond lengths are about 9 a.u.

A qualitatively new situation occurs when the interaction of four Be atoms in a tetrahedral geometry is considered. The stability of the cluster is 20-50 kcal/mole depending on the AO basis set used, but in any case it is much larger than that found for the other trimers and tetramers. The equilibrium distances are close to 4.2 a.u. (the internuclear separation present in Be crystal) corresponding to a deep minimum in the potential energy curve. At this internuclear separation the tetrahedral Be_4 is strongly stabilized by the sp hybridization. A second shallow minimum is present at larger distances and is due to the van der

Waals forces operating between Be atoms in their $2s^2$ atomic configurations already observed in the previously described Be_3 and Be_4 clusters. The potential energy curve with the two minima is generally characteristic of all Be clusters where a significant s-p hybridization is effective.

Planar Be_7 is the first Be cluster with a considerable stability containing no tetrahedral unit. This cluster is a part of the (0001) crystal plane of the hcp Be crystal. The data of population analysis, based on the natural orbitals, confirm a large participation of the in-plane p orbitals to the bonding.

The extension of two-dimensional Be structures allows a delocalization of the bond over many atomic centers, resulting in a large stabilization of the cluster. Planar $Be_{10}(10,0)$ and $Be_{13}(13,0)$ are in fact not unfavourable with respect to the more compact geometries containing the basic tetrahedral subunit, such as $Be_{10}(7,3)$ or $Be_{13}(3,7,3)$.

The nature of the bonding in small Mg and Ca aggregates is not different from that of very small Be clusters, e.g. Be_2 , Be_3 , square and rhombic Be_4 . In contrast to the Be case, also tetrahedral Mg_4 and Ca_4 do not display a significant stability if basis set without d-functions are used. Only when d-functions are included in the basis set and when simultaneously correlation effects are considered, the Mg_4 and Ca_4 tetrahedral arrangements display a small stability which amounts to 11 and 14 kcal/mole, respectively. Once again the equilibrium bond distances (6.4 a.u. for Mg_4 and 8.1 a.u. for Ca_4) are similar to the nearest neighbor distances present in the respective Mg hcp lattice (6.1 a.u.) and Ca fcc lattice (7.5 a.u.).

In a recent study on the nature of the bonding in Be_4 , Mg_4 and Ca_4 clusters, Bauschlicher, Bagus and Cox (199) have obtained results and conclusions parallel to ours. Because they have formulated the reasons for the different behaviour of considered systems in a very clear way we summarize in the following their arguments. The different stabilities found in both tetrahedral molecules and respective metals are attributed to the different degree of hybridization. In particular, it was suggested that the Mg-Mg bond

is weaker than the Be-Be one because of the more diffuse nature of the 3p orbital in comparison with the 2p one. The experimental atomic excitation energies are in fact very similar in Be and Mg ($21\,878\text{ cm}^{-1}$ and $21\,850\text{ cm}^{-1}$, respectively (249)).

On the other hand, the smaller atomic excitation energy of Ca, $15\,158\text{ cm}^{-1}$, compensates the more diffuse nature of the 4sp hybrid bonding orbital of Ca with respect to the 3sp hybrid of Mg, so that these two competing effects are almost cancelled. The existence of a low-lying $4s^1 4d^1$ (3D) excited state in Ca can explain the slightly larger stability of Ca_4 with respect to Mg_4 . Moreover, Bauschlicher, Bagus and Cox have found that in the larger $\text{Mg}_{13}(3,7,3)$ aggregate the central Mg atom presents a very large increase of the sp population with respect to the Mg_4 case, indicating that the number of nearest neighbors can largely influence the nature of the bonding in these systems (199).

2.5.2.3 Aluminium clusters

The electronic structures of Al clusters are markedly different from those of the previously discussed alkali and alkaline-earth metal clusters. In the case of rhombic Al_4 , for example, the four lowest valence MOs are mainly combinations of s valence orbitals as in the case of Li_4 . In rhombic Al_4 , however, all these bonding and antibonding MOs are completely filled while in the analogous Li_4 cluster only two are doubly occupied and the others are virtuals. The contribution to the bonding due to the interaction of s AOs in Al_4 is therefore very small as compared to Li_4 . The stability of Al clusters is largely caused by the interaction of p AOs.

The most stable Al tetramer has a rhombic geometry, but the differential electron density map for this cluster does not give evidence for the three-center-bond found in the analogous Li_4 cluster (Fig. 2.5.3) Moreover, the deformation of rhombic Al_4 into square Al_4 occurs without strong changes in the electronic structure as well as in the energy of the system. The differential electron density map for square Al_4 (Fig. 2.5.4) demonstrates that the kind of bonding in this cluster is similar to that

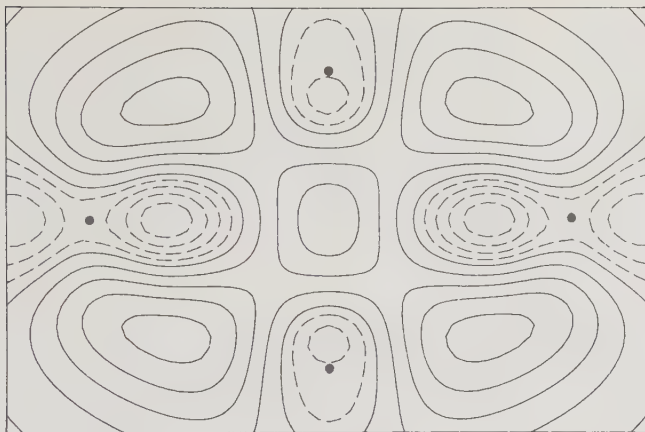


Fig. 2.5.3 - Differential electron density map for rhombic Al_4 (see Fig. 2.5.1 for definitions).

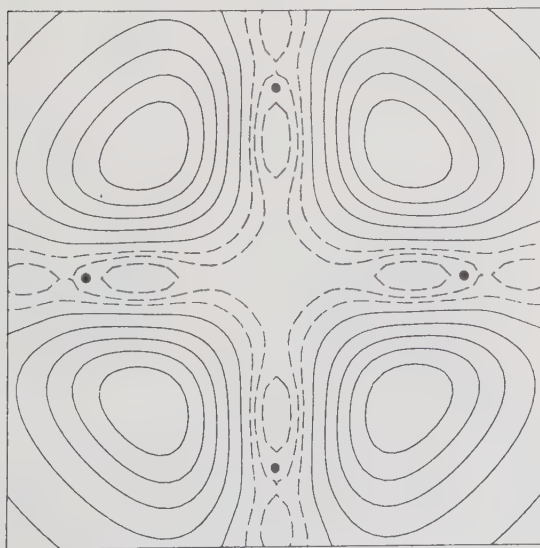


Fig. 2.5.4 - Differential electron density map for square Al_4 (see Fig. 2.5.1 for definitions).

of the rhombic structure (Fig. 2.5.3).

In general, most stable Al clusters are segments of the Al fcc crystal lattice, but the deformability of these structures to give geometrical arrangements of different symmetry can be considered a characteristic of this group of clusters.

Finally, the formation of the bond in the Al clusters causes an sp hybridization which increases the $3s^1 3p^2$ character of the Al atoms.

2.5.2.4 Germanium clusters

Germanium crystallizes in the diamond-like structure with a Ge-Ge nearest neighbor distance of 4.63 a.u. . However, the Ge clusters do not display structures which can be considered sections of the diamond crystal lattice. In fact, the most stable Ge tetramer has a rhombic geometry like in the case of alkali metal clusters. Whiteside et al. (252) have shown that also in the case of C_4 clusters the rhombic arrangement is the preferred one. Tetrahedral C_4 and Ge_4 are higher in energy not only with respect to the rhombus, but also in comparison with other tetra-

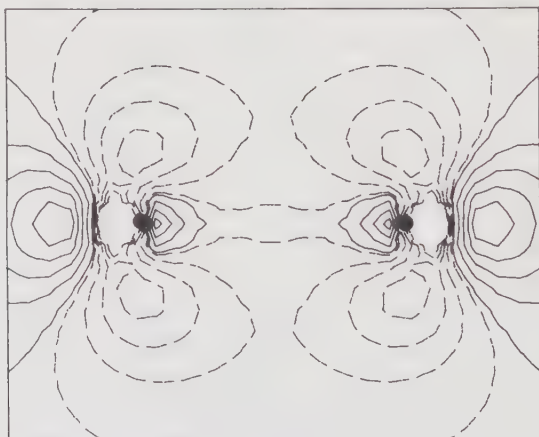


Fig. 2.5.5 - Differential electron density map for the xz plane (short diagonal) of rhombic C_4 (see Fig. 2.5.1 for definitions). The map shows a lowering of the electron density in this region of the cluster.

atomic structures such as square and T-shaped Ge_4 clusters or linear or T-shaped C_4 clusters (250,252).

In both C_4 and Ge_4 rhombic structures the bond is mainly due to the interaction between in-plane p-orbitals. The predominance of the σ -type bonds lying in the plane of the rhombus is demonstrated for the C_4 cluster by the existence of a negative region in the electron density map plotted in the plane in which the short diagonal lies and which is perpendicular to the rhombus plane (Fig. 2.5.5).

The qualitatively similar bonding present in square and rhombic C_4 and Ge_4 is shown by the corresponding differential electron density maps (Figs 2.5.6-7-8-9).

Among Ge clusters containing a larger number of atoms (5, 6 and 7), the structures which are sections of the diamond-like crystal lattice are less stable than other more compact agglomerates. As for Li clusters, some planar Ge clusters show stabilities comparable to those of structures containing a larger number of bonds.

However, the largest value of the binding energy per atom is that of the pentagonal bipyramid Ge_7 , confirming the existence of very stable clusters with five-fold symmetry.

The MO energy level diagrams of Ge_4 clusters show that the MOs arising from the interaction of 4p orbitals are clearly separated from the MOs originating from the interaction of s AOs. On the contrary, a similar analysis for the rhombic C_4 cluster indicates the presence of a very small gap between the two groups of MOs (250). This can be considered as a reason for the larger involvement of p-orbitals in the bonding of the systems containing elements of the first-row of the periodic table.

The population analysis for Ge clusters indicates that the four valence electrons of the Ge atoms undergo only a small electronic redistribution which corresponds to an average population $4s^{1.8}4p^{2.2}$ in the molecular state. The electronic structure of small Ge clusters, therefore, looks very different from that of the Ge crystal where the bond is due to the overlap of the sp^3 hybrid orbitals centered on each Ge atom.

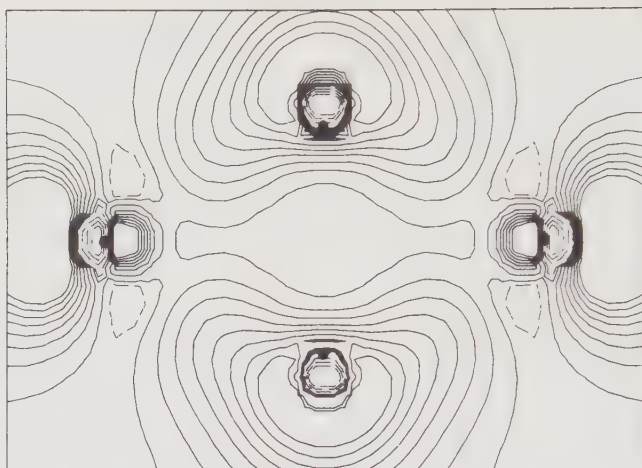


Fig. 2.5.6 - Differential electron density map for the xy plane of rhombic C_4 (see Fig. 2.5.1 for definitions). The map shows an accumulation of electron density in the plane containing the carbon atoms.

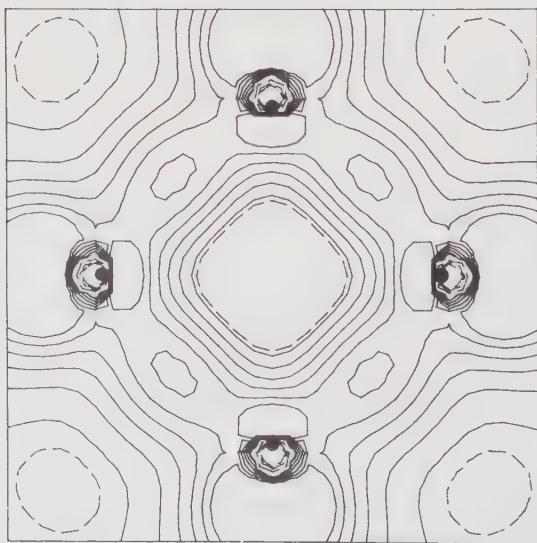


Fig. 2.5.7 - Differential electron density map for square C_4 (see Fig. 2.5.1 for definitions).

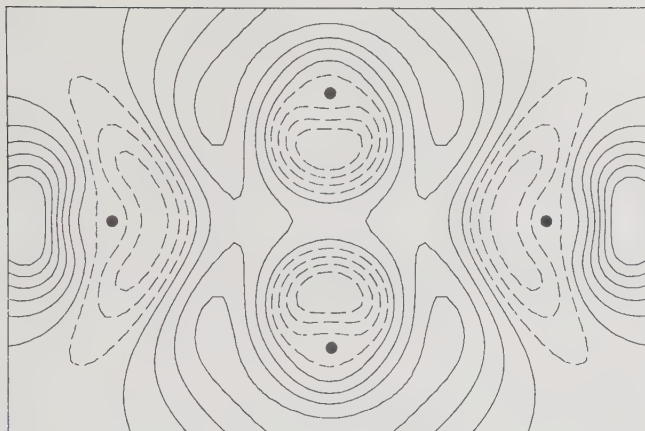


Fig. 2.5.8 - Differential electron density map for rhombic Ge_4 (see Fig. 2.5.1 for definitions).

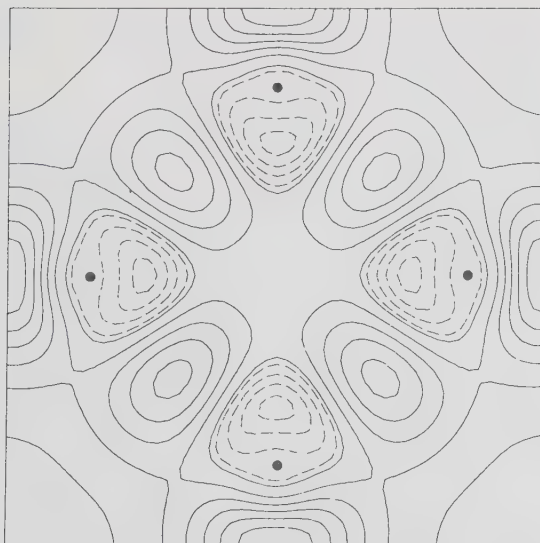


Fig. 2.5.9 - Differential electron density map for square Ge_4 (see Fig. 2.5.1 for definitions).

2.5.3 Spin multiplicity of small clusters

The spin properties of small clusters can largely influence their stability. The proper consideration of the correlation effects is therefore fundamental for the investigation of the ground states of clusters. Usually, the configuration interaction procedure lowers the energy of states of lower spin multiplicity more than the energy of states with higher multiplicity. Therefore, the ordering of the states predicted on the basis of the one-electron approximation is very often reversed after inclusion of correlation effects.

2.5.3.1 Group Ia clusters

In general, the SCF calculations indicate very small energy differences between the lowest singlet and triplet (or doublet-quadruplet) electronic configurations for these clusters. The CI treatments yield more frequently the singlet or the doublet as the ground state of alkali metal clusters. For many structures, however, the two lowest singlet and triplet (or doublet and quadruplet) states are nearly degenerate and the splitting between the two states is a few kcal/mole.

A second characteristic recognizable in alkali metal clusters is the appearance of a biradical behaviour in some cases; if there are in the one-electron approximation two degenerate non-bonding MOs occupied with only two electrons the system can display a biradical character. The occupation numbers of the natural orbitals can be taken as the criterion for the biradical feature when the correlation effects are taken into account.

The geometry variation from rhombic (singlet ground state) to square (triplet ground state) Li_4 clusters changes the spin multiplicity but this cluster deformation is accompanied by only a moderate change in energy.

The relatively low stability of the clusters with biradical character can cause higher reactivity of such clusters and therefore an enhanced capability to interact with other atoms or molecules as opposed to clusters with no biradical character (137).

2.5.3.2 Group IIa clusters

With the exception of linear Be_3 , which is characterized by a bonding triplet ground state, small alkaline-earth metal clusters show always a closed shell ground state electronic configuration. The first medium-size Be agglomerate for which a triplet ground state was found is the planar Be_7 . In this case, the $^3\text{B}_{1g}$ ground state is separated by a few kcal/mole from a second triplet state, $^3\text{B}_{2u}$ and from the first singlet state, $^1\text{A}_g$.

The tendency to exhibit small singlet-triplet splitting becomes more evident with increasing cluster size. For the Be_{13} clusters the two lowest singlet and triplet states are nearly degenerate and the exact definition of the ground state of the system is questionable, depending on the details of the calculation and on the choice of the geometrical parameters.

The existence of clusters having triplet ground states separated by small energy gaps from the lowest singlet states can be considered as a symptom of a developing metallic character.

2.5.3.3 Aluminium clusters

Differently from the case of alkali metal clusters, for which ground states of the lowest possible spin multiplicity are usually found, small Al clusters have always triplet or quadruplet ground states. In both linear and triangular Al_3 the quadruplet state lies below the first doublet state. In all tetramers considered, square, rhombus, T-form and tetrahedron, the ground state is a triplet and for the two pentamers square pyramidal and bipyramidal trigonal, a quadruplet ground state was found. In some cases, however, the splitting between the two states of low and high spin multiplicity is relatively small.

The reason of the appearance of high-multiplicity ground states in Al clusters has to be looked for in the existence of a set of MOs very close in energy originated by the interaction of 3p orbitals.

These MOs cannot be fully occupied by the valence p-electrons. The energy necessary to couple the spins seems to exceed the energy gap existing between these energy levels so that the final state is a multiplet.

2.5.3.4 Germanium clusters

As for the alkali metal clusters the most stable Ge structures are always characterized by a singlet ground state. States of higher multiplicity, triplets or quintuplets, are more typical for strained or for highly symmetrical structures.

The case of rhombic and square Ge_4 is of particular interest. The transition from the singlet closed shell state of the rhombus to the triplet state of square Ge_4 with the modification of the geometry is due to the gradual approach of the HOMO and LUMO of the cluster resulting in the degenerated MOs in the D_{4h} symmetry. The consequence is that square Ge_4 is a typical biradical structure as confirmed by the analysis of the natural orbitals. A full analogy between the pseudo Jahn-Teller effects in Li_4 and Ge_4 is therefore observed.

2.5.4 Cluster stability

2.5.4.1 Group Ia clusters

The computed binding energy per atom (BE/n) in Li clusters grows rapidly with the increasing size of the agglomerate. The value of the BE/n should approach the experimental cohesive energy of lithium crystal (38 kcal/mole) if the number of nearest neighbors approaches the value 8.

The plot of the BE/n values against the average number of nearest neighbors (n_b) for the most stable Li clusters for given number of atoms n indicates that the increase in stability in clusters which are sections of the fcc lattice and for clusters with five-fold symmetry is practically linear (Fig. 2.5.10). A similar result was found for clusters which model the (100) and (110) surfaces of bcc Li lattice (137).

Obviously, the binding energy per Li atom depends on many factors (cluster geometry, spin multiplicity), but the behaviour of the BE/n with the increasing average number of nearest neighbors proves that the bond character in compact metals can be understood on the basis of cluster calculations.

Going from Li to the higher alkali metal elements it is pos-



Fig. 2.5.10 - Dependence of the binding energy per atom on the average number of nearest neighbors (n_b) for the most stable fcc Li clusters $\text{Li}_2 - \text{Li}_8$ (top of the figure) and for the Li_6 and Li_7 cluster with pentagonal symmetry.

sible to observe a regular decrease of the cluster stability. The BE/n of the rhombic arrangements, computed with the PP MRD CI method, are in fact 14.3, 8.0 and 4.4 kcal/mole for Li_4 , Na_4 and K_4 , respectively. This is in qualitative agreement with the decreasing cohesive energies of the alkali metals which are (in kcal/mole) 38.0 for Li, 26.0 for Na and 21.7 for K.

Taking into consideration that the introduction of d-functions in the AO basis set increases the D_e of K clusters for about 50 per cent, it is possible to estimate the true value of BE/n of rhombic K_4 to be about 6-7 kcal/mole. The ratios of the stabilities in the case of bulk metals and clusters are therefore very similar.

2.5.4.2 Group IIa clusters

Be_2 , Be_3 and some Be_4 and Be_5 clusters are weakly or extremely weakly bonded species. However, the fact that metallic Be exists and that the cohesive energy of metallic beryllium (78 kcal/mole) is even larger than the cohesive energy of metallic lithium (38 kcal/mole) indicates that the bond strength must change dramatically when larger Be agglomerates are formed.

As previously discussed, these changes are mainly due to the sp hybridization occurring in small clusters (e.g. tetrahedron) when the geometrical structure allows a pronounced directionality of the bond or when large clusters are considered. This process is associated with a drastic increase of the cluster stability. The plot of the BE/n against the average number of nearest neighbors of the cluster clearly shows this effect (Fig. 2.5.11).

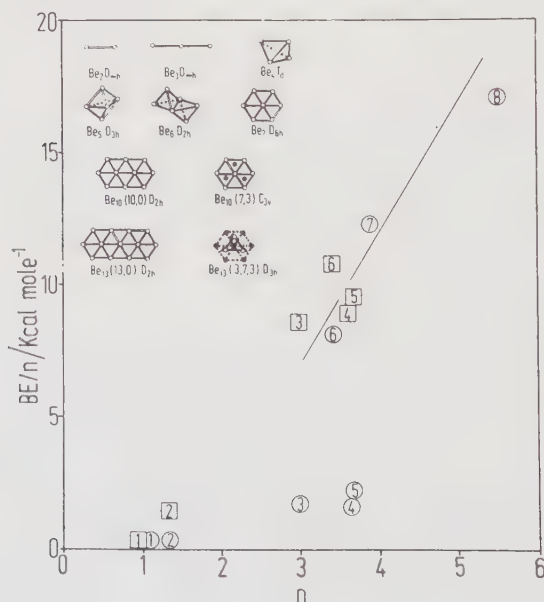


Fig. 2.5.11 - Dependence of the binding energy per atom on the average number of nearest neighbors (n) for most stable Be clusters. Square and circles indicate results obtained with basis set $|4s4p/4s2p|$ and $|4s4p/2s1p|$, respectively (1) Be_2 ; (2) Be_3 ; (4) Be_5 ; (5) Be_6 ; (6) Be_7 ; (7) $\text{Be}_{10}(10,0)$; (8) $\text{Be}_{13}(3,7,3)$.

The values of BE/n obtained employing the smaller basis set (Fig. 2.5.11) indicate a very rapid increase of the cluster stability only for the biggest clusters, Be_7 , Be_{10} and Be_{13} . This is due to the relatively poor description of the s-p interaction. However, with the increase of the dimensions of the cluster the stabilities computed with the two basis sets tend to approach each other.

Differently from Group Ia metal clusters, in the case of alkaline-earth metal aggregates the stability of clusters of the same size and geometry does not change regularly in the series Be, Mg, Ca. The values of BE/n for the tetrahedral Be, Mg and Ca tetramers, computed with comparable basis sets including d-functions, are 12.0, 3.0 and 3.5 kcal/mole, respectively. The corresponding cohesive energies of the metals are 78.3, 35.3 and 42.4 kcal/mole.

2.5.4.3 Aluminium clusters

The cohesive energy of metallic aluminium is identical to that of Be (78 kcal/mole) but, differently from alkaline-earth metal clusters, aluminium clusters display a considerable stability already for small size structures. The trend concerning the binding energy per atom with the increasing number of Al atoms is not regular enough to extrapolate to larger systems. In fact the values of BE/n are 13.6, 15.8 and 14.3 kcal/mole for clusters containing 3, 4 and 5 Al atoms, respectively.

An investigation of larger Al clusters is necessary in order to find a convergence of the values of BE/n to the metallic cohesive energy.

2.5.4.4 Germanium clusters

Ge clusters are certainly the most stable ones among the clusters here considered. The experimentally determined dissociation energies demonstrate this fact as well (235, 236).

Although the computational method adopted accounts only for ~ 50-60 per cent of the experimental dissociation energy (only valence electrons are correlated and a basis set without d-functions was used) we found that the rhombic Ge_4 , with a BE/n of

36.1 kcal/mole, is much more stable than all other tetramers of the elements here considered.

Nevertheless, the experimental behaviour of the BE/ n with the increasing cluster size is qualitatively reproduced by the present calculations (Fig. 2.4.12). In particular, the value of BE/ n grows very rapidly for the first members of the series ($2 \leq n \leq 4$) and quite slowly for larger Ge clusters ($4 \leq n \leq 7$). In order to understand the high cohesive energy of the Ge crystal (90 kcal/mole) drastic changes in the electronic structure are expected when larger Ge aggregates are formed.

2.5.5 Conclusions

The electronic properties computed for the tetramers of Groups Ia, IIa, IIIa and IVa at the highest level of theory used are summarized and compared with respective crystal data in Table 2.5.1.

From the previous discussion and the Table 2.5.1 it is possible to draw general qualitative conclusions about analogies and differences existing between small clusters and crystals.

- 1) Small homonuclear clusters of metallic elements (Li, Na, K, Be, Mg, Ca, and Al) which crystallize in more compact crystal structures, e.g. bcc, fcc or hcp, display some basic properties found in the metal crystals. In particular: a) the most stable clusters are slightly deformed sections of the corresponding crystal lattices; b) clusters exhibiting five-fold symmetry (e.g. pentagonal bipyramid) are also very stable and can be considered as first steps in a pentagonal crystal growth. The possible existence of stable clusters with regular or distorted icosahedral geometry is supported by the experimentally observed "magic numbers" in the mass spectra of clusters of various elements; c) the equilibrium bond lengths found in the clusters are always close to the nearest-neighbor separation present in the metal; d) the same electronic effects which cause the stability of the metal are effective also in small clusters (e.g. the different amount of sp hybridization in alkaline-earth metal clusters); e) the binding energy per atom as a function of the increasing number

Table 2.5.1 - Comparison between computed electronic properties of M_4 clusters and experimental data for crystals

	M_3 cluster					Crystal			
	Method	Basis ¹⁾ set quality	Optimal geometry	Ground state	$R_{M,M}$ (a.u.)	E_g /atom (kJ/mol)	Crystal lattice	Nearest neighbor distance (a.u.)	Cohesive energy (kJ/mol)
<i>Group IA</i>									
Li	AE	TZ + 2p	D_{2h}	1A_g	5.8	54.4	bcc	5.7	159.0
Na	AE	TZ + 2p	D_{2h}	1A_g	6.6	45.2	bcc	6.9	108.8
K	PP	QZ + 2p + 1d	D_{2h}	1A_g	8.9	23.8	bcc	8.6	90.8
<i>Group IIA</i>									
Be	AE	DZ + 2p + 1d	T_d	1A_1	4.2	50.2	hcp	4.2	321.7
Mg	PP	QZ + 2p + 1d	T_d	1A_1	6.4	12.6	hcp	6.1	147.7
Ca	PP	QZ + 2p + 1d	T_d	1A_1	8.1	14.6	fcc	7.5	176.1
<i>Group IIIA</i>									
Al	PP	DZ + 1d	D_{2h}	$^3B_{1u}$	5.2	76.6	fcc	5.4	321.7
<i>Group IVA</i>									
C	AE	DZ + 1d	D_{2h}	1A_g	2.7	361.9	Diamond	2.9	711.3
Ge	PP	TZ + 1d	D_{2h}	1A_g	4.8	139.3	Diamond	4.6	373.6

¹⁾ DZ = double zeta, TZ = triple zeta, QZ = quadruple zeta, p = p-polarization function, d = d-polarization function.

of atoms in the cluster tends to the value of the cohesive energy of the crystal. Whereas the increase of the stability of alkali metal clusters starts already at very small cluster sizes, the binding energy per atom begins to grow very strongly only for medium size alkaline-earth clusters. This different behaviour of the cluster stability is due to the different role of the p-polarization functions in the chemical bonding in the alkali and alkaline-earth metal clusters: only in the Group IIa clusters in fact the p orbitals are appreciably involved in the sp hybridization. Consequently a minimum optimal geometrical configuration of Group IIa clusters is necessary to allow for the stabilizing overlaps between sp-hybrids of neighboring atoms in the cluster sufficiently to influence the overall binding energy.

Therefore, the same kind of bonding exists in metal clusters and metal crystals. The surface reconstructions of the bcc metal can be connected with the larger stability of two-dimensional fcc lithium clusters in comparison with bcc structures. In general, more compact geometrical configurations seem to be preferable for clusters which are systems with a large share of surface atoms.

One can conjecture that a tendency exists for the regions near to the crystal surface to take geometrical forms corresponding to a most closed packed structure possible.

2) Clusters of elements which crystallize in a diamond-like structure (e.g. C and Ge) behave differently from the previously described clusters of metal atoms. In particular: a) structures which can be recognized as sections of the diamond-like lattice are less stable than more compact cluster geometries; b) the kind of electronic redistribution at the atoms of the cluster is very different from the sp^3 hybridization of the atoms in the crystal. The formation of sp^3 hybrid orbitals occurs only when the energy gained with the formation of a sufficient number of bonds compensates the excitation energy required for the transition $ns^2np^2 \rightarrow ns np^3$; c) the convergence of the binding energy per atom of Ge to the sublimation energy of the crystal is slow.

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4. APPENDIX: ABBREVIATIONS, SYMBOLS, UNITS

AE	All Electron
AO	Atomic Orbital
a.u.	atomic unit (1 a.u. of energy = 1 hartree, 1 a.u. of distance = 1 bohr)
bcc	body centered cubic
BE/n, E_B/n	Binding Energy per atom
CEPA	Coupled Elelctron Pair Approximation
CI	Configuration Interaction
CNDO	Complete Neglect Differential Overlap
CSF	Configuration State Function
D_e	Dissociation Energy
DF	Density Functional
DIM	Diatomic In Molecule
ESR	Electron Spin Resonance
fcc	face centered cubic
GTO	Gaussian Type Orbital
hcp	hexagonal close packing
HOMO	Highest Occupied Molecular Orbital
IP	Ionization Potential
LCAO	Linear Combination of Atomic Orbitals
LEED	Low Electron Energy Diffraction
LUMO	Lowest Unoccupied Molecular Orbital
MCD	Magnetic Circular Dichroism
MO	Molecular Orbital
MRD CI	Multi Reference Double excitation Configuration Interaction
nM/mR	number n of main configurations M and of roots R in the MRD CI treatment
NO	Natural Orbital
PP	Pseudopotential
SCF	Self Consistent Field
STO	Slater Type Orbital
T	selection threshold in the MRD CI treatment
TEM	Transmission Electron Microscopy
UHF	Unrestricted Hartree Fock

UV	Ultraviolet
VB	Valence Bond
X_α	Slater X_α approximation

Energy conversion table

	hartree	kcal/mole	kJ/mole	eV	cm^{-1}
hartree	1	$6.275 \cdot 10^2$	$2.622 \cdot 10^3$	27.210	$2.195 \cdot 10^5$
kcal/mole	$1.594 \cdot 10^{-3}$	1	4.18	$4.336 \cdot 10^{-2}$	$3.497 \cdot 10^2$
kJ/mole	$3.813 \cdot 10^{-4}$	$2.392 \cdot 10^{-1}$	1	$1.037 \cdot 10^{-2}$	83.66
eV	$3.675 \cdot 10^{-2}$	23.061	96.39	1	$8.066 \cdot 10^3$
cm^{-1}	$4.556 \cdot 10^{-6}$	$2.859 \cdot 10^{-3}$	$1.195 \cdot 10^2$	$1.240 \cdot 10^{-4}$	1

Distances conversion

$$1 \text{ bohr} = 5.2916 \cdot 10^{-11} \text{ m} = 0.52916 \text{ \AA}$$

ABSTRACT

The electronic structure and the properties of small clusters of Groups Ia, IIa, IIIa and IVa have been investigated by means of pseudopotential and all electron Hartree-Fock calculations followed by configuration interaction.

The results can be summarized as follows:

- 1) Small homonuclear clusters of metallic elements (Li, Na, K, Be, Mg, Ca, and Al) which crystallize in more compact crystal structures, e.g. bcc, fcc or hcp, display some basic properties found in the metal crystals. In particular: a) the most stable clusters are slightly deformed sections of the corresponding crystal lattices; b) clusters exhibiting five-fold symmetry (e.g. pentagonal bipyramid) are also very stable and can be considered as first steps in a pentagonal crystal growth; c) the equilibrium bond lengths found in clusters are always close to the nearest-neighbor separation present in the metal; d) the same electronic effects which cause the stability of the metal are effective also in small clusters (e.g. the different amount of sp hybridization in alkaline-earth metal clusters); e) the binding energy per atom as a function of the increasing number of atoms in the cluster tends to the value of the cohesive energy of the crystal. Whereas the increase of the stability of alkali metal clusters starts already for very small cluster sizes, the binding energy per atom begins to grow very strongly only for medium size alkaline-earth clusters. This different behaviour of the cluster stability is due to the different role of the p-polarization functions in the chemical bonding in the alkali and alkaline-earth metal clusters: only in the Group IIa clusters in fact the p-orbitals are appreciably involved in the sp hybridization.
- 2) Clusters of elements which crystallize in a diamond-like structure (e.g. C and Ge) behave differently from the previously described clusters of metal atoms. In particular: a) structures which can be recognized as sections of the diamond-like lattice are less stable than more compact cluster geometries; b) the kind of electronic redistribution at the atoms of the cluster is very different from the sp^3 hybridization of the atoms in the crystal; c) the convergence of the binding energy per atom of Ge to the sublimation energy of the crystal is slow.

ZUSAMMENFASSUNG

Die elektronischen Strukturen und die Eigenschaften von kleinen Metallclustern der Elementgruppen Ia, IIa, IIIa, und IVa wurden untersucht mit der Pseudopotential- sowie mit der All-Elektronen Hartree-Fock Methode und anschließender Berechnung der Konfigurationswechselwirkung.

Die Ergebnisse können folgender massen zusammengefasst werden:

- 1) Kleine homonucleare Cluster der metallischen Elemente (Li, Na, K, Be, Mg, Ca, und Al), welche in kompakteren Strukturen kristallisieren, z.B. bcc, fcc oder hcp, zeigen einige grundsätzliche Eigenschaften, die in Metallkristallen gefunden werden. Im einzelnen: a) die stabilsten Cluster sind die, welche eine etwas deformierte Teileinheit des zugehörigen Kristallgitters darstellen; b) Cluster mit pentagonaler Symmetrie (z.B. pentagonale Bipyramide) sind ebenfalls sehr stabil, und man kann annehmen, dass sie als erste Schritte im pentagonalen Kristallwachstum dienen; c) Die Gleichgewichtsbindungs-längen der Cluster sind immer sehr ähnlich denen, die man bei der Nächste-Nachbarn Trennung in Metall erhält; d) die gleichen elektronischen Effekte, welche die Stabilität der Metalle ausmachen, wirken auch in kleinen Clustern (z.B. der unterschiedlicher Betrag der sp-Hybridisierung in Erdalkalimetall-Clustern); e) die Bindungsenergie pro Atom als Funktion der ansteigenden Anzahl der Atome in Cluster tendiert zum Wert der Cohäsiven Energie des Kristalls. Obwohl das Ansteigen der Stabilität von Alkalimetall-Clustern schon bei sehr kleiner Clustergrösse beginnt, wächst die Bindungsenergie pro Atom für Erdalkalimetall-Cluster erst dann stark an, wenn sie eine mittlere Grösse erreicht haben. Dieses unterschiedliche Verhalten der Cluster-Stabilität beruht auf der unterschiedlichen Rolle der p-Polarisationsfunktionen in der chemischen Bindung von Alkali- und Erdalkalimetall-Clustern: nur bei Clustern der Gruppe IIa sind die p-Orbitale wesentlich an sp-Hybridisierung beteiligt.
- 2) Cluster der Elemente, welche in einer diamantähnlichen Struktur kristallisieren (z.B. Kohlenstoff und Germanium) verhalten sich anders als die zuvor beschriebenen Cluster der Metallatome. Im einzelnen: a) Strukturen, welche als Teile des diamantähnlichen Gitters aufgefasst werden können, sind weniger stabil als die kompakteren Cluster-Geometrien; b) die Art der Elektronenverteilung in den Atomen des Clusters ist sehr verschieden von

der sp^3 -Hybridisierung der Atome des Kristalls; c) im Falle von Germanium konvergiert die Bindungsenergie pro Atom langsam zum Wert der Sublimationsenergie des Kristalls.

QUELLENNACHWEIS

Mit der pauschalen Genehmigung des Vorsitzenden des Fachbereichs-rates des Fachbereichs Chemie vom 30.4.1976 wurden Ergebnisse der vorliegenden Arbeit zu folgenden Gelegenheiten veröffentlicht:

- /1/ G. Pacchioni, H.O. Beckmann and J. Koutecký, "Investigation of alkali metal clusters with multireference double-excitation configuration interaction method", Chem. Phys. Letters 87, 151-158 (1982).
- /2/ G. Pacchioni and J. Koutecký, "The bond nature of alkaline-earth homonuclear metal clusters investigated with pseudo-potential CI method", Chem. Phys. 71, 181-198 (1982).
- /3/ G. Pacchioni and J. Koutecký, "On the nature of the bonding in Mg_4 and Ca_4 clusters", J. Chem. Phys. 77, 5850-5851 (1982).
- /4/ G. Pacchioni, "Applicability of a pseudopotential CI method to the investigation of ground and excited states of molecular systems: $NaCO$, Li_2H , Al_2 and AlH ", Theoret. Chim. Acta 62, 461-475 (1983).
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